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Bench-Scale Investigation of Composting for Remediation of Explosives-Contaminated Soils from Iowa Army Ammunition Plant, Middletown, Iowa

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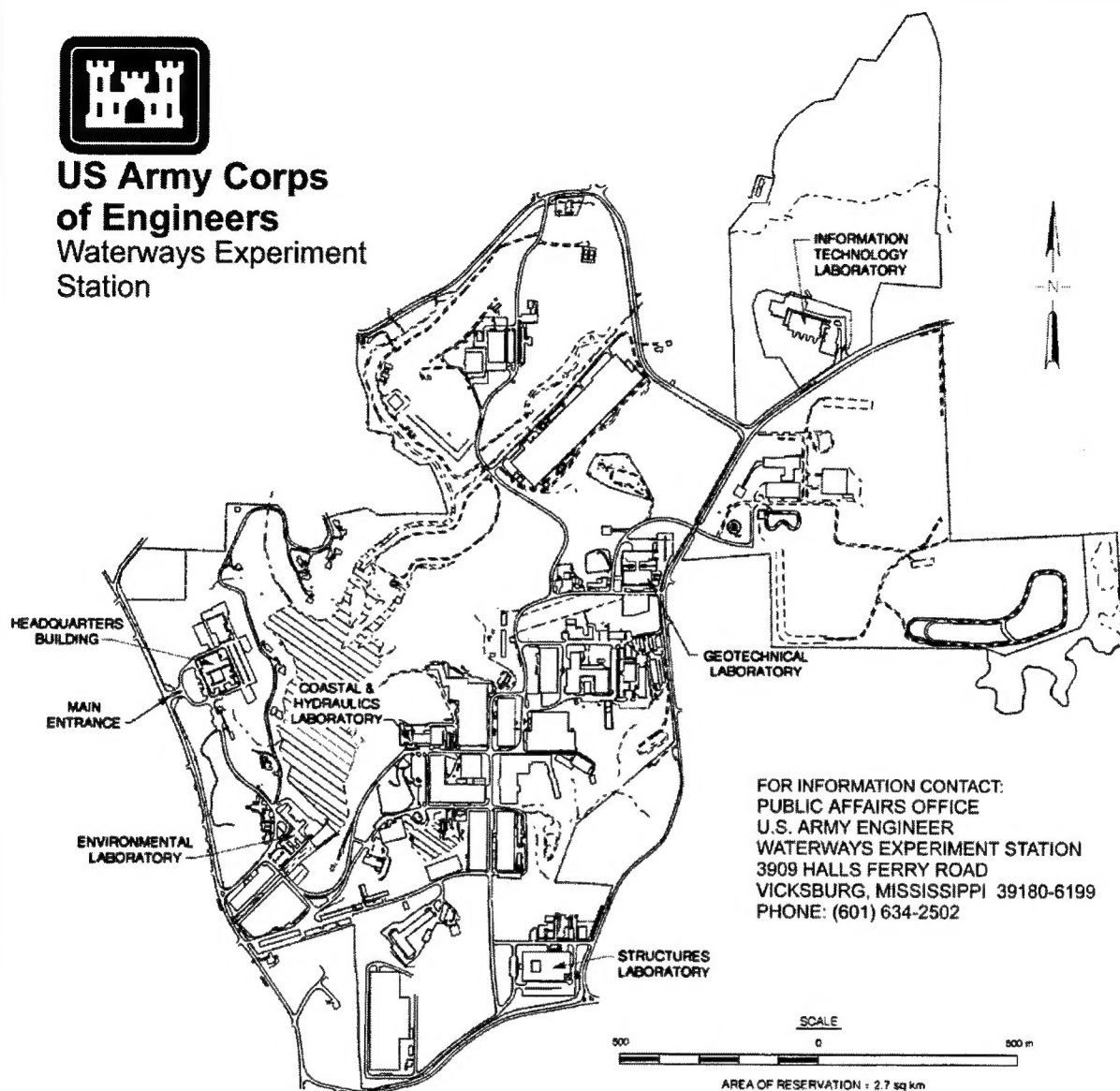
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Preface

The study herein was conducted as a part of the Bench Compost Implementation Study. This report was prepared at the U.S. Army Engineer Waterways Experiment Station (WES) in cooperation with the Iowa Army Ammunition Plant (IAAP), Middletown, IA, and the U.S. Army Corps of Engineers, Omaha District. Program Manager for IAAP was Mr. Leon Baxter. Program Manager for the Omaha District was Mr. Kevin M. Howe. Project Managers for WES were Dr. Kurt T. Preston and Mr. Roy Wade.

The bench-scale studies were conducted between October 1994 and July 1996 in the WES Environmental Laboratory (EL). This report was written by Dr. Kurt T. Preston and Mr. Roy Wade, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), EL, WES; Dr. Kyoung S. Ro, Louisiana State University; Mr. Steve Seiden, North Carolina State University; and Dr. Mary Bergess, University of Toledo. Mr. James Davis, Contract Student from Mississippi State University, provided laboratory support.

The report was prepared under the direct supervision of Mr. Daniel E. Averett, Chief, ERB, and under the general supervision of Mr. Norman R. Francingues, Jr., Chief, EED, and Dr. John Harrison, Director, EL.

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1 Introduction

The manufacturing process of conventional munitions has resulted in the generation of explosives-contaminated soils at various military installations. The principal explosive contaminants are 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,4-triazine (RDX), and octhydro-1,3,5,7-tetranitro-1,3,5,7-triazine (HMX). The Iowa Army Ammunition Plant (IAAP) is one of many military installations that provide materials to the Army's weapon systems. The production operations of these weapons used explosive materials and lead-based initiating compounds (Jaycor 1993).

Because of the potential for groundwater contamination and the subsequent migration of explosives, treatment of the explosives-contaminated soils at several sites at IAAP is necessary to protect the environment and avoid costly actions in the future. Incineration and composting are demonstrated technologies for the remediation of explosives-contaminated soils. However, incineration is publicly undesirable and essentially economically unfeasible for remediation of small sites. Composting was the selected technology that was evaluated for the remediation of the explosives-contaminated soils at IAAP. The results of the bench-scale study are presented.

Background of IAAP

The IAAP is located in Middletown, IA, 140 km (87 miles) southwest of Davenport, IA, 167 km (104 miles) west of Peroria, IL, and 121 km (75 miles) south of Iowa City, IA (Figure 1). IAAP daily operations are managed by Mason and Hanger-Silias Company, Incorporated, under the guidance of the U.S. Army Armament, Munitions, and Chemical Command, Rock Island, IL. IAAP has provided manufacturing support to the Army for the production of ammunition items since 1941. IAAP is currently operating to load, assemble, and pack ammunition items, including projectiles, mortar rounds, warheads, demolition charges, antitank mines, antipersonnel mines, and the components of these munitions, including primers, detonators, fuses, and boosters. The loading, assembling, and packaging operations use explosive materials and lead-based initiating

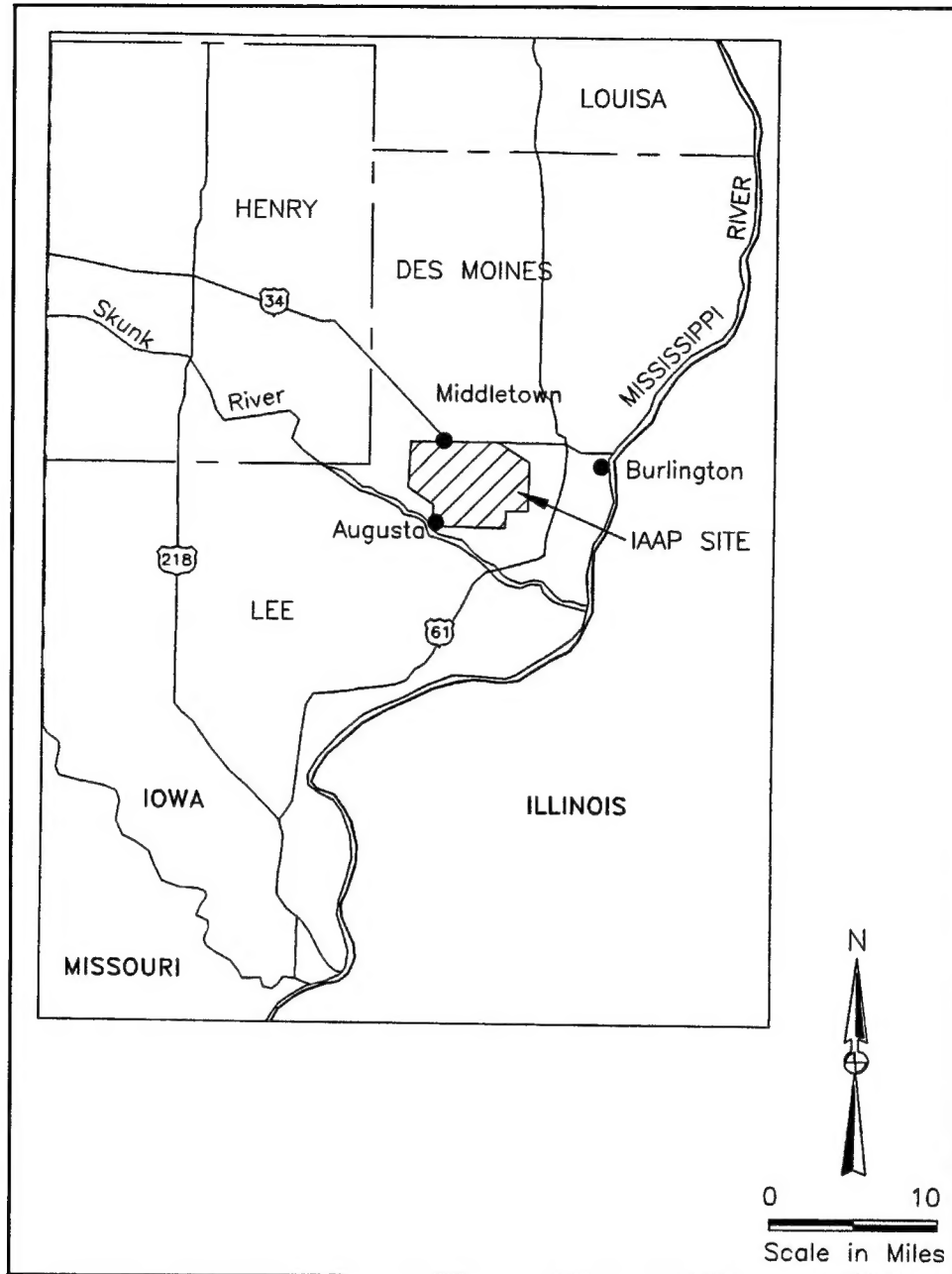


Figure 1. Site location map of IAAP (Source: Dames and Moore)

compounds (Jaycor 1993). The munition production at IAAP has resulted in the discharge of wastewater containing explosives and explosive by-products to the installation's surface waters, including holding ponds and impoundments. Figure 2 shows the location of each site.

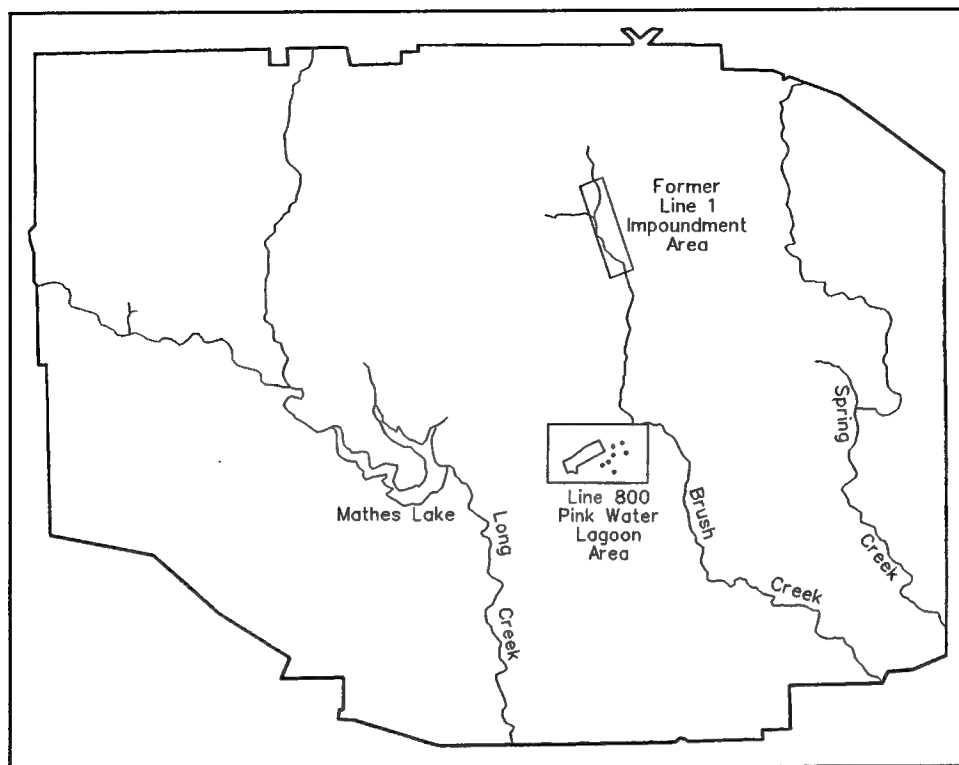


Figure 2. Location of former Line 1 Impoundment and Line 800 Pink Water Lagoon areas (Source: Dames and Moore)

Site History

Former Line 1 Impoundment

The Line 1 facilities parallel the upper reaches of Brush Creek in the northeastern portion of the IAAP installation. Large quantities of explosive waste and pink water have been reported from Line 1 facility during the period of 1948 to 1975. To control the effluent discharge problem in 1948, a 396-m (1,300-ft) continuous embankment covering 1.5 ha (3.6 acres) was constructed along the upper reaches of Brush Creek (Dames and Moore 1989). This embankment was breached after 1975 and is now inhabited by overgrown vegetation and small trees. During high streamflow, the impoundment may reach 732 m (2,400 ft) upstream covering 3.0 ha (7.5 acres) (SCS 1982).

The geology of the former Line 1 Impoundment was characterized by shallow borings in the vicinity of the site. The sediment material was classified as sandy, silty clay till, and silty clay loess at depths of 0.6 to 1.5 m (2 to 5 ft) deep. Limestone outcrops have been observed in the creek valley south of the former Line 1 Impoundment (Dames and Moore 1989).

Line 800 Pink Water Lagoon

The Line 800 Pink Water Lagoon, constructed in the 1960s, borders Line 800 and an intermittent tributary to Brush Creek. The lagoon spans 2.0 ha (5 acres) and is 1.2 m (4 ft) deep. The lagoon operated as an unlined waste site for the effluent from Line 800 and sludge from different processes around the IAAP installation. The lagoon was an active disposal site from 1943 to 1995. The majority of the waste disposed of in the lagoon was from washdown activities, metal cleaning, and plating operations at facilities from Line 800 (Dames and Moore 1989). The lagoon is currently not in use and holds accumulated sediments and standing water. According to Dames and Moore (1989), the lagoon was later used as a settling pond to reduce particulate prior to discharge into Brush Creek.

The geology of the Line 800 Pink Water Lagoon is characterized from boreholes drilled into bedrock in the vicinity of the site. The overburden consists of 6.1 to 17.7 m (20 to 58 ft) of clay-rich till with some sand and silt. The clays in the overburden are very stiff with relatively low permeability. A layer of sand ranging from 3.4 to 5.8 m (11 to 19 ft) thick was encountered. The bedrock underlying this area consists of fossiliferous limestone interbedded with layers of shaley clay and silt. The bedrock surface appeared weakened, and the upper portion of the limestone bedrock exhibits enhanced permeability (Dames and Moore 1989).

Site Contamination

Soils at the Former Line 1 Impoundment and Line 800 Pink Water Lagoon sites were tested for explosives, metals, and other organic analytes. These compounds and elements are known to have carcinogenic, mutagenic, or other adverse effects on living organisms.

Former Line 1 Impoundment

The soil at the Former Line 1 Impoundment had elevated levels of explosives. Explosive contaminants detected were RDX at concentrations ranging from 4 to 400 mg/kg and HMX ranging from 1.4 to 61 mg/kg. The HMX concentration was not significant, since the action level is 51,000 mg/kg. The action levels for TNT, RDX, and 1,3,5-trinitrobenzene (TNB) were 196, 53, and 102 mg/kg, respectively. Even though the explosive concentrations decreased laterally along the creek, elevated concentrations were measured as far as 23 m (75 ft) west of the creek for HMX and 366 m (1,200 ft) for RDX. Sampling on the east side of the creek was limited due to drill rigs along the creek. Therefore, symmetrical contamination was assumed on the east bank. All contamination seemed to be contained within the first 1.2 m (4 ft) of soil. The total volume of contaminated soil along Brush Creek was estimated to be 29,437 m³ (38,500 yd³).

In addition, the soil was sampled for metals (i.e., copper, cadmium, and lead), and no significant concentrations were detected.

Line 800 Pink Water Lagoon

The surrounding soils and sediments at the Line 800 Pink Water Lagoon have elevated levels of explosives and perhaps other organic analytes. Explosive contaminants detected were RDX at a concentration of 800 mg/kg, HMX at 110 mg/kg, 2,4,6 TNT at 2,000 mg/kg, and TNB at 200 mg/kg. The highest concentration of explosives was detected in a former sludge dumping area, located in the southwest portion of the lagoon. These contaminants exceeded the action limit except for HMX. The significant contaminant concentration appeared within the first 0.6 m (2 ft) of the lagoon. Beyond 0.6 m (2 ft), the concentration dropped with depth, and no contamination was detected beyond 3 m (10 ft). The total volume of contaminated soil estimated at the Line 800 Pink Water Lagoon was 25,232 m³ (33,000 yd³). Unfortunately, the lagoon is storing 6.2×10^6 L (1.63×10^6 gal) of water that requires removal prior to initiation of any soil remediation process. The water is also considered to be contaminated with RDX and TNT.

Purpose

The purpose of this report is to document and present the results of the respirometric, bench-scale composting, and TNT radiolabeled tests performed as a part of the comprehensive remediation composting study. The results of this study will be provided to assist with the design of a pilot-/field-scale remediation compost system at IAAP.

Testing Objectives

The objective of this study was to evaluate and select the best combination of amendments, contaminated soils, and bulking agents to be utilized in the composting technology for remediating soils contaminated with the explosives TNT, HMX, and RDX. The objective of the respirometric test was to provide a general indication of biological activity within each compost mixture. Respirometry also was used as a tool for the specific screening of compost mixtures for the IAAP soil. The objective of the bench-scale compost reactor test was to extend the respirometric study, evaluating the applicability of the screened compost mixtures for degrading explosive compounds under actual composting environments prior to the pilot-/field-scale implementation. The objective of the radiolabeled study was to provide insight into the apparent degradation of the explosive contaminant during the composting process.

Scope of Work

The scope of work includes a survey of locally available sources of amendment and bulking agents to be used for testing on the former Line 1 Impoundment and/or Line 800 Pink Water Lagoon soils and collection of soil samples at these sites. An initial screening of eight compost mixtures was performed to determine if any biological activity will occur using the respirometer and to select an optimum compost mixture for further evaluation. The bench-scale compost test was run to further validate the respirometric test results under actual composting environments. The University of Minnesota investigated the degradation of TNT using the selected mixture and the radiolabeled method.

2 Remediation Composting Process Parameters

Successful design and operation of the remediation composting requires careful consideration of numerous factors affecting the process. The factors can be divided into three classes: physical, chemical, and biological. Physical factors define the structure of the compost matrix. Chemical factors consider the adequacy of substrates and the toxic effects of contaminants on the compost biomass. Biological factors define biodegradability and the biodegradation rate. Careful choice of a composting system with proper thermodynamic properties ensures the optimal thermophilic conditions (Preston, Seiden, and Ro 1997).

Physical Factors

Porosity

Porosity is a measure of pore or void space between solid particles in a bed and is defined as the ratio of void volume to the total bed volume in a system. It may be represented as a fraction or on a percentage basis. Porosity is important in compost systems for a number of reasons. The pore space provides a conduit for nutrient movement through the compost pile, space for the growth of microbial communities, and a reservoir for moisture held in the compost mixture.

The gas/liquid ratio has a profound impact on the efficiency of the compost operations and the efficacy of the treatment process. When the pore space is completely filled with water, oxygen within the system may become limited, and the compost system will become anaerobic. Also, the physical strength of the compost matrix will be undermined. Although this example is extreme, it highlights the importance of the interaction of solid particles, pore space, and the free airspace (FAS) in the definition of the physical nature of the compost matrix.

Free airspace

The FAS is the ratio of the empty pore space (V_a), or void volume not occupied by water, to the total volume. FAS is that portion of the pore space that is occupied by gas phase. Research indicates that the optimal biological activity occurs with an FAS ranging from 0.20 to 0.35 (Haug 1993). FAS is critical for the movement of oxygen and other gases into and through the compost matrix by either diffusion, convection, or forced ventilation.

The FAS may be managed by selection of the amendments and bulking agents, which are perhaps two of the most critical design decisions. The selection of these influence the nature of the compost, the efficiency of the operation, and the economics of the system.

In general, FAS begins to become available within the pore space in most compost systems at approximately 40-percent solids (Haug 1993; Golueke 1991). Thus, 40-percent solid content is generally considered as the maximum for most compost systems without augmentation by forced aeration.

Moisture content

An understanding of the role of water in compost design is of paramount importance. Beyond the role of water as a biochemical solvent, water in compost systems has an even larger multifaceted role. Water plays a key role in the cooling of compost systems. Also, moisture content influences the nutrient movement and the compost matrix structure.

As a biochemical solvent, aqueous solutions are theoretically the ideal media for biological activity. In a completely mixed aqueous system, substrate is instantly available to the microbial community in equal concentration. When nutrients are added to the system, the biomass will be active and immediately utilize the available substrate. However, in aqueous aerobic systems, oxygen is often the limiting substrate due to its low solubility in aqueous solutions. Aqueous bacterial reactor systems generally attempt to improve oxygen transfer into solution by physical agitation or sparging of air.

Compost, a highly active aerobic system, can also suffer from oxygen limitation. As a result, proper management of the air and water within the compost pore volume is critical.

The optimal moisture content reported by researchers varied from 45 to 90 percent (Biddlestone et al. 1987; Haug 1993). The reported optimal moisture content varied because of the widely varying water absorption capacity of soil particles and composting materials used in research (Mathur 1991). Generally, a moisture content of about 45 to 65 percent is used. Above this range, the pore space will be filled with water, or at the

very least, water tension in the pore space hinders the movement of gases between pores so that oxygen in the pore space becomes depleted. Below this range, moisture is not available to the microbial communities. The water remaining becomes associated with the solid particles due to the matrix potential arising from the capillary forces and adsorption. This water is held so tightly that it may be unavailable for utilization by microbes. Consequently, moisture may be present in the matrix, but the lack of moisture available to the microbial communities results in growth-rate limitations and a loss of process efficiency.

Particle size

Various shredders and other mixing devices are used to break down and homogenize the compost materials into smaller and manageable sizes. Since most of the composting microbial activities occur on the surface of the substrate particles, smaller size particles, which offer larger surface area, appear to enhance the microbial reactions. However, the movement of oxygen and water may be hindered in narrow interstitial spaces between the small particles packed together tightly. Generally, particle sizes between 1.3 and 5.0 cm are used for composting (Forster and Wase 1987). Small particles are used for forced-aeration compost systems, and large particle sizes are appropriate for windrow systems.

Temperature

Temperature is an important indicator in composting. As the microorganisms in a compost degrade organic substrates, heat is generated as a by-product of microbial breakdown of the organic substrate raising the compost temperature to the desired thermophilic conditions. Microbial activities and chemical reactions are usually faster at higher temperatures. For municipal solid wastes (MSW), retention of heat is also necessary in order to sanitize the wastes. The retention and continual generation of heat are dependent upon the configuration, size, and insulating property of composting systems, ambient temperature, and the heat values of substrates. Although higher temperature is beneficial in many ways, the microorganisms and enzymes are inactivated, and the composting process will stop beyond 70 °C. Above 60 °C, most mesophiles, including fungi, will be destroyed or inactivated, and the decomposing activity is carried out mainly by actinomycetes. After readily available substrates such as starches, sugars, lipids, and proteins have been consumed, the compost temperature will fall below 60 °C and will allow fungi and actinomycetes to attack cellulose and lignin portions of the substrates. Recently, researchers agreed that 55 to 60 °C is the optimal temperature range (Bollen 1985; Finstein and Miller 1985).

Chemical Factors

Contaminated soil loading

The economics of composting systems is primarily based on the amount of contaminated soil processed during a given time period. The higher the ratio of contaminated soil in a unit volume of compost given an equivalent microbial activity, the lower the overall cost of the system on a unit basis. However, this economic incentive must be carefully balanced with the possible inhibition by the contaminants on the compost of microbial activities and for the decrease in compost temperature simply due to replacing organic substrates with mostly inert soil. Loading the system with an excess of inhibitory contaminant slows microbial activity and results in an increase of composting time or may cause a total process upset. As a result, the composting process may not be able to reach or maintain a stable thermophilic state for the desired reaction time due to lack of organic substrates.

Carbon to nitrogen ratio (C/N)

Compost microorganisms require adequate levels of carbon (C) sources and nutrients including nitrogen (N), phosphorous, sulfur, and other trace minerals and growth factors. Among these, C and N are usually the limited substrates, while other elements and nutrients are abundant in composting processes. Chemical elemental analysis of soil microorganisms revealed that the cells in general contain about 50-percent C, 5-percent N, and 0.25- to 1-percent phosphorous on a dry weight basis (Alexander 1977). Assuming about one-half to two-thirds of the carbon is converted to carbon dioxide (CO₂) and the rest to cell mass, the required C/N ratio would be about 23 to 35. The optimal C/N ratios for different composting materials range from 20 to 35 (Haug 1993).

If the initial C/N ratio is too high (i.e., low nitrogen level), the microorganisms pass through many life cycles to achieve a stable state (i.e., C/N of about 10). This may not be desirable for conventional MSW composting because it reduces the substrate stabilization rate. It may, however, be beneficial for remediation composting because dead microorganisms themselves are organic substrates and support endogenous activities for long periods. If the C/N ratio is too low, nitrogen will be lost as ammonia, which may reach toxic levels and raise the pH of the compost mix. For a compost mix with high C/N ratio, ammonia-releasing substrates such as blood, urine, or urea can be added. If phosphorous and other nutrient concentrations are low, as in cases of using industrial solid wastes as substrates, these elements need to be supplemented in order to avoid unnecessary rate limitations.

pH

pH of the compost matrix must be near neutral (i.e., pH of 7). For all practical purposes, microbial growth is severely limited at pH values less than 3 or greater than 11. The optimum pH of composting has been reported to be between 6.0 and 8.5 (Fitzpatrick 1993). At higher pH (strongly basic), ammonium ions (nitrogen source) are lost as ammonia, and essential elements such as calcium and magnesium may not be available to microorganisms due to precipitation as insoluble metal hydroxides or carbonates. At lower pH (strongly acidic), toxic metals, aluminum, copper, zinc, etc., leach from minerals and substrates and may stop the composting process.

Overall, compost mix pH may be adjusted with cosubstrates or other pH-adjusting chemicals such as lime and baking soda if the initial pH falls outside the optimum range. For instance, wood wastes and sludges from pulp and paper mills may have a low pH of 5 to 6 and high C/N. Addition of ammonia-releasing substrates such as urine or urea will neutralize the acidity and provide necessary nitrogen to microorganisms. Fortunately, composting has the unique ability to buffer both high and low pH to a neutral range as composting proceeds. This phenomenon may be explained by the release of carbon dioxide (CO_2) and ammonia (NH_3) as a result of organic decomposition. Therefore, pH adjustment is usually not required and is not a common practice in composting systems.

Biological Factors

Biodegradability and biodegradation rate

Substrate biodegradability determines the amount of substrate energy available to drive the composting process, the requirement for additional energy amendments, the stoichiometric oxygen demand, the air demand to remove heat from the process, and the final product mass. Literature values for biodegradability of substrates vary widely; for instance, 28 percent for steer manure to 68 percent for chicken manure (Klein 1972) or 21.7 percent for newsprint to 81.9 percent for food wastes (Kayhanian and Tchobanoglous 1992). Chandler et al. (1980) reported that the lignin content was the single most important factor influencing the biodegradability of a compost system.

In contrast to MSW, which requires a long retention time (typically more than 90 days of composting) to achieve adequate stabilization, long retention time may not be required nor desired for remediation of soils contaminated with explosive compounds. Most of the previous remediation composting studies indicated that less than 30 days were required to substantially degrade or transform TNT, RDX, and other explosive compounds by aerobic composting (Doyle and Isbister 1982; U.S. Army Toxic

and Hazardous Material Agency 1988; Garg, Grasso, and Hoag 1991; Pennington 1995).

Aeration

Aeration is important in two aspects: oxygen supply to aerobic microorganisms and cooling/drying of the compost by evaporation of water. For nonmechanical aeration systems, oxygen may be transported via molecular diffusion and free convection of air movement due to temperature gradients. Oxygen may also be supplied by forcing air through the compost matrix or mechanically mixing the compost intermittently to enhance oxygen transfer. Aeration is also used to dry and subsequently cool the compost by promoting evaporation of water. Approximately 10 to 30 times more aeration is required for drying of 20-percent solids than for biological oxidation (Haug 1993). Composters typically use about 1 m³ air/kg volatile solids-day.

3 **Respirometric Study**

Introduction

Respirometry is a technique for determining oxygen consumption in an aerobic environment (Mahendraker and Viraraghavan 1995) under conditions that avoid rate limitations from lack of nutrients, oxygen, moisture, imbalanced pH, or inadequate seed microbes. During aerobic respiration, microbial activity results in mineralization of organic matter into CO₂ and water, as well as utilization of the substrate as a carbon and energy source for cell growth and maintenance. Monitoring of respiration rates in microbial populations or biomass is a useful tool for measuring the biodegradation of organic matter, that has been applied to wastewater treatment, composting, and bioremediation.

Respirometry, as mentioned earlier, provides biodegradation rates, the rates at which microorganisms degrade different organic substrates (Flathman and Nowakowski 1995; Carlsson 1993; Vanrolleghem and Verstraete 1993; Kappeler and Gujer 1992; Grady et. al. 1989). Respirometric data can be used to approximate the short-term biochemical oxygen demand (SBOD) and oxygen uptake rate (OUR) and to estimate the standard biochemical oxygen demand (Spanjers, Olsson, and Klapwijk 1994; Vanrolleghem and Spanjers 1994; Jacobi and Fussa 1993). In addition, respirometry helps to identify the toxic and inhibitory effects that the organic substrate may have on the microorganisms (Boening, Hendricks, and Rossignol 1995; Spanjers, Temmink, and Klapwijk 1994; Herricks et al. 1991).

Finally, respirometry can be used as a tool for determining treatment plant design parameters for sizing blowers, aerators, and composting piles (Hunter, Johnson, and Carns 1995; Brouwer, Klapwijk, and Keesman 1994; Arthur and Meredith 1993; Klapwijk, Spanjers, and Temmink 1993; Watts and Garber 1993; Rozich and Guady 1992). Several reviews are available that discuss different techniques and applications for respirometry (Mahendraker and Viraraghavan 1995; Arthur and Arthur 1994). To date, no significant research has been conducted on using a respirometry to provide insight on contaminated soils, in particular, soils contaminated with explosives (Mahendraker and Viraraghavan 1995).

In this study, a respirometric technique was used as a first step to determine the optimal compost mix for treating explosives-contaminated soils from the Rockeye site. Eight compost mixtures were evaluated for their total oxygen utilization and uptake rates as well as the degradation of TNT, HMX, RDX, 4-amino-2,6-dinitrotoluene (4A-DNT), and 2-amino-4,6-dinitrotoluene (2A-DNT).

Materials and Methods

Soil samples

A 97-L (25-gal) sample consisting of five 20-L (5-gal) buckets was collected from the vicinity of the Former Line 1 Impoundment Lagoon (latitude 40°48.32'N and longitude 91°13.61'W) at an approximate elevation of 205 m (674 ft). Three definite soil horizons were observed. Horizon A₁ was a dark sandy loam soil approximately 20 cm (8 in.) thick. Horizon A₂ was a layer of red-colored soil of the same texture less than 2.54 cm (1 in.) thick. The red color was presumed indicative of explosive contamination. As a result, this layer was inferred to contain the highest level of contamination. Horizon B appeared to be a clay soil. Given the gray mottled appearance of Horizon B, it was further presumed that the soil is often in a state of oxygen-reducing conditions. Three 20-L (5-gal) bucket samples were taken from Horizons A₁ and A₂; two 20-L (5-gal) bucket samples were taken from the Horizon B. TNT field kits confirmed the presence of explosive contaminants.

Upon receipt at the U.S. Army Engineer Waterways Experiment Station (WES), the sample was air-dried and homogenized using a Gilson splitter. Agglomerations were crumbled, but not pulverized using a pestle. The total sample weight after homogenization was approximately 90 kg. Consolidation allowed the samples to be placed within four 20-L (5-gal) sealed buckets. The homogenized sample was classified as a loam to silty loam using the hygrometric particle size determination (sand - 31.8 percent, silt - 49.4 percent, colloidal clay - 8.36 percent, and noncolloidal clay - 10.4 percent). The physical characteristics of Lagoon 800 and Line 1 Impoundment soils are presented in Table 1.

From the homogenized bulk sample, a subsample was dry-sieved and characterized for the contaminant concentration found in each fraction of sand, silt, and clay. The results indicated the explosive concentrations in each of the fractions of sand, silt, and clay. Table 2 shows the totals of explosive concentration of Line 1 Impoundment soil that appear to be representative of the contaminants found at the site.

Table 1
Physical Characteristics of Lagoon 800 and Line 1 Impoundment Soils

Physical Properties (Lagoon 800/Line 1 Impoundment)					
Color (Munsell Soil Color Chart)			2.5 YR 4/2, Dark Grayish Brown/5 YR 2.5/1, Black		
pH			3.50/6.21		
Average Densities of Fractions (oven-dried at 60 °C) (Lagoon 800/Line 1 Impoundment)					
Sample Description			Average Density, g/cc		
Bulk < 2.00 mm, dry sieved			2.59/2.57		
Bulk < 0.85 mm, dry sieved			2.58/2.57		
Bulk < 0.85 mm, wet sieved			2.60/2.57		
Sample Fractions (Lagoon 800/Line 1 Impoundment)					
Dry-Sieve Analysis (2,171.35/2,655.32 g as-Is and 2,047.38/2,542.10 g Dry Wt.)					
Sieve Fraction	Raw Wt., g	Solids per 1-g Sample	Oven-Dried Wt., g (Moisture Test)	Percent Dry Fraction	
> 2.00 mm	0.22/20.34	1.0000/0.9862	0.22/20.06	0.01/0.79	
0.063 - 2.00 mm	1851.97/1914.94	0.9347/0.9596	1730.99/1837.40	84.55/72.28	
< 0.063 mm	299.14/582.5	0.9574/0.9646	286.41/561.88	13.99/22.10	
Gain (Loss)	(20.02/137.54)	—	(29.76/122.76)	(1.45/4.83)	
Wet-Sieve Analysis (2,601.39/2,830/63 g as-Is, 2,152.35/2,607.71g Dry Wt.), 19.0 L rinse water					
> 2.00 mm	3.82/16.12	0.7853/0.9218	3.00/14.86	0.14/0.57	
0.063 - 2.00 mm	211.10/822.33	0.6796/0.7667	143.47/630.51	6.67/24.18	
0.0025 - 0.063 mm	2112/1767.6	111.2/196.4 g/L	2065.23/1806.0	88.4/69.3	
< 0.0025 mm	—	—	—	—	
Gain (Loss)	—	—	(59.15/156.34)	(2.75/5.99)	
Moisture Tests (oven-dried at 60 °C)					
Sample	Initial Wt., g	Dry Wt., g	Percent Moisture	Percent Solids	
Bulk > 2.00 mm dry-sieved	0.22/2.90	0.22/2.86	0.00/1.38	100/98.62	
Bulk < 0.063 mm dry-sieved	6.21/8.76	5.95/8.45	4.26/3.54	95.74/96.46	
Bulk > 2.00 mm wet-sieved	3.74/0.51	2.94/0.47	21.39/7.84	78.61/92.16	
Hydrometer Procedure					
Time	Temp., °F	Hydrometer Reading		Reading Correction	
0 hr	92.3/73.4	—		—	
40 sec	92.3/73.4	35.0/33.0		39.9/34.1	
2 hr	72.5/69.8	11.0/9.0		11.9/9.4	
24 hr	68.9/68.9	6.5/4.0		6.7/4.2	
Percent (Silt + Clay)	Percent Sand	Percent Silt	Percent Clay (Coll + Noncoll)	Colloidal Clay	Noncolloidal Clay
79.7/68.1	20.3/31.8	55.9/49.4	23.8/18.7	13.4/8.4	10.4/10.4
USDA Classification: Silty Loam/Loam to Silty Loam					

Table 2
Explosive Results - IAAP Line 1 Impoundment Soil

Contaminant, mg/kg	Sand	Silt	Clay	Total
TNT	5.8	3.4	2.2	11.4
HMX	4.9	33.8	64	102.7
RDX	32.9	332	278	642.9

Compost mixtures

From previous studies, WES determined that to characterize each compost treatment, total oxygen utilization and oxygen uptake rates for IAAP soil must be measured. Eight compost mixtures were evaluated, and two optimal compost mixtures were selected for the bench-scale composting experiment. Ingredients for these mixes are shown in Table 3. Each compost mixture used in the initial study contained by volume (v/v) 20 percent manure, 65 percent amendment, and 15 percent IAAP Line 1 Impoundment soil by wet weight. The amendments were cow and swine manures, while the bulking agents included cornstalks, sawdust, and woodchips. The compost mixes had C/N ratios ranging from 28 to 62, moisture contents ranging from 52 to 65 percent, and pH ranging from 6.3 to 7.6 (Table 3).

Table 3
Respirometric Result - Composition and Physiochemical Properties of the Compost Mixtures

Mixture Number	Amendment and Bulking Agents	pH	Percent Moisture	TVS	TKN	C/N Ratio
1	Cow manure and sawdust	6.91	52.31	84.8	5548	42
2	Swine manure and sawdust	6.43	57.43	60.7	4210	40
3	Cow manure and cornstalk	7.06	65.52	70.1	7029	28
4	Swine manure and cornstalk	7.27	64.19	70.9	4791	41
5	Cow manure and sawdust/cornstalk	7.13	55.66	60.9	5245	32
6	Swine manure and sawdust/cornstalk	6.44	61.39	78.0	4572	47
7	Cow manure and woodchips	7.55	59.72	70.5	5011	39
8	Swine manure and woodchips	6.28	52.76	68.6	3077	62

Respirometer procedure

A BI-1000 Electrolytic Respirometer (Bioscience, Inc., Bethlehem, PA) was used to collect oxygen-utilization data. This respirometer consisted of eight 1-L reactor bottles, a reactor module, a water bath (40 °C), a temperature controller, a personal computer, and control software. Approximately 200 ml of each mix was placed into a flask. The initial amounts of total volatile solids (TVS), total Kjeldahl nitrogen (TKN), TNT, RDX, HMX, 4A-DNT, and 2A-DNT for each treatment were determined by analyzing a portion of the remaining mix.

After 10 days, the compost was removed from each bottle and analyzed for final amounts of explosive, TVS, TKN, pH, and moisture content. The half-life of each mix was calculated to determine which mix most effectively removed the explosives from the soil. In addition, the final respiration data were used to estimate the amount of oxidized carbon, which was later used to determine the substrate degradation rate and the specific biodegradation rate (SBR) of each mix (Table 4).

Table 4
Respirometric Biodegradation Kinetic Coefficients of the Compost Mixtures

Mixture Number	Total Oxygen Consumed, g	Maximum OUR, g/day	Degraded Organic-C, g	Initial Organic-C, g	Substrate Degradation Rate Coefficient Day ⁻¹	SBR day ⁻¹
1	2.22	0.664	0.81	10.44	0.008	0.008
2	1.00	0.674	0.36	7.90	0.005	0.005
3	3.60	1.006	1.31	5.72	0.026	0.023
4	4.25	2.610	1.55	11.19	0.015	0.014
5	3.95	0.991	1.44	7.04	0.023	0.020
6	3.91	1.928	1.42	7.16	0.022	0.020
7	3.00	1.217	1.09	10.23	0.011	0.011
8	3.50	1.383	1.27	7.90	0.018	0.016

Physicochemical parameters

Oxygen utilization. The BI-1000 was programmed to record data every 30 min. This respirometer incorporates a potassium hydroxide trap to remove the CO₂ respired by the biomass, resulting in the change of the pressure inside the flask. The change in pressure is proportional to oxygen utilization. The oxygen utilized was replaced with oxygen produced by electrolysis of water at 100 mg per hour. The oxygen replacement was computer controlled.

Oxygen uptake rate. OURs were determined from the oxygen utilization data collected by the BI-1000 respirometer. OURs were calculated by dividing the change in oxygen by the time interval for a specific change.

Moisture content. The moisture content was determined by oven-drying the compost at 104 °C for 24 hr, subtracting the final weight from the initial weight, and dividing the result by the initial weight (Greenburg, Clesceri, and Eaton 1992).

Total volatile solid. The TVSs were determined by placing the compost sample into a furnace at 550 °C, subtracting the final weight from the initial weight, and dividing the result by the initial weight (Method 2540G Total, Fixed, and Volatile Solids and Semisolid Samples; Greenburg, Clesceri, and Eaton 1992).

Total Kjeldahl nitrogen. Three to five grams of compost were mixed together with 5 ml of sulfuric acid in a 250-ml polyethylene bottle. After agitating the bottle for 3 min, 245 ml of double-distilled water was added. Twenty milliliters of sample was digested using a BD-46 Digester. After digestion, the TKN values were measured on a Lachat instrument using QuikChem method 10-107-06-02-D.

Specific biodegradation rate. The SBR was calculated by dividing the grams of degraded carbon as CO₂ by the grams of initially available carbon in dry weight and by the days of incubation. A similar method was described by Atkinson et al. (1996). The total amount of dry weight carbon can be estimated as follows (Haug 1993):

$$\text{Dry Weight C} = (\text{TVS}/1.8) * \text{Dry Weight} \quad (1)$$

The mole ratio of O₂ consumed to CO₂ generated was about 16.5/16, and this ratio was used to estimate CO₂ generation based on O₂ consumption data.

pH. Approximately 5 g of compost was mixed into a slurry using two to three times the amount of distilled deionized (DDI) water. The mixture was stirred twice before measuring it with a pH meter.

C/N Ratio. The carbon-to-nitrogen ratio was calculated using the following equation:

$$\text{C/N} = \text{biodegradability factor} * (\text{TVS}/1.8) \div (\text{TKN} * 10^{-4}) \quad (2)$$

The biodegradability factor is assumed to be 0.5 (Haug 1993). The percent available nitrogen is the TKN value divided by 10,000.

Explosive analysis

Explosives were determined by SW846 Method 8330: Nitroaromatics and Nitroamines by high performance liquid chromatography (HPLC) (U.S.Environmental Protection Agency (USEPA) 1992). Samples were homogenized by stirring and extracted without drying. Chromatographic analysis was performed with a Perkin Elmer Integral 4000 HPLC using a C-18 Reverse Phase HPLC column (Supelco LC-18), 25 cm by 4.6 mm (5 μ m). Extraction was performed using acetonitrile.

Half-life estimations for explosives

The half-life estimations were determined by assuming the first-order equation,

$$k = \ln(C_o/C_t)/t \quad (3)$$

where,

k = first-order rate coefficient, days⁻¹

C_o = initial contaminant concentration, mg/kg

C_t = contaminant concentration at time t , mg/kg

t = composting time, days

Equation 3 was solved for k . The half-life (days) was then estimated from Equation 4.

$$t_{1/2} = 0.693/k \quad (4)$$

where $t_{1/2}$ equals half-life (days).

Results and Discussion

The IAAP soil was analyzed for explosives, but the explosive concentrations were low. Based on WES's experience, the biodegradation rates of each mix should display the same trends as long as the concentration of explosives does not inhibit microbial activity (Preston, Seiden, and Ro 1997). Therefore, the compost treatment was evaluated for SBR and OUR.

Table 4 displays the SBRs, the maximum OUR, and the first-order SBR coefficients. The SBR for each mixture was determined from the accumulated oxygen data from the respirometer. Mixture 3 had the highest SBR of 0.023 day⁻¹ and Mixture 2 had the lowest of 0.005 day⁻¹. From this data, the first choices for treatment to be considered would be Mixes 3, 5,

and 6. However, Mixture 4 had the highest OUR of 2.6 g per day followed by Mixtures 6-8. Interestingly, Mixtures 3 and 5, which contain cow manure and cornstalk, had the highest SBR, while the mixtures that contain swine manure and cornstalk, Mixtures 4 and 6, had the highest OURs.

The substrate degradation rate coefficients ranged from 0.005 to 0.026 day⁻¹. Haug (1993) reworked a correlation for the substrate degradation rate coefficient at various temperatures for composting a mixture of garbage and dewatered, digested sludge cake as:

$$k_d = 0.00632 * (1.066)^{T-20} \quad (4)$$

where

k_d = rate coefficient, day⁻¹

T = temperature, °C

Equation 4 using 40 °C of the respirometric test temperature predicts k_d of 0.023 day⁻¹, which is within the rate coefficient range.

Eight compost mixtures were evaluated for their substrate utilization rates and degradation rates of explosive analyte and transformation products found in the IAAP soils. Compost Mixes 3 (cow manure, cornstalk, and soil) and 4 (swine manure, cornstalk, and soil) showed the fastest degradation potential for the explosives. Compost Mixture 3 showed the best biodegradation rate, and Mixture 4 showed the best respiration rate, while its biodegradation rate falls approximately in the middle of the eight treatments.

Although Mixture 6 (pig manure, cornstalk, and sawdust) was among the highest in terms of SBR and OUR, it was not selected because of the extra bulking agent ingredient. However, Mixture 6 may be effective in treating the explosives-contaminated soil.

4 Bench-Scale Composting Study

Introduction

The preliminary success of the compost Mixtures 3 and 4 from the respirometric test was further evaluated under actual composting environments. A bench-scale remediation composting system that closely simulates the actual composting process was used to expand the respirometric study. The bench-scale study is expected to provide the preliminary feasibility, the fate of the contaminants, and the health risk of composted products. The pilot-scale studies can be initiated to cover the scale-up factors and the heterogeneity of field conditions, and finally successful field operations can be implemented.

The standard composting method of ASTM D5338 uses incubators to externally control the compost reactors at predefined temperatures (35 °C for the first 16 days and 55 °C for 28 days). With this externally predefined temperature control, reproducibility of data may be improved; however, many leading experts argue that it may not adequately represent the actual composting process in which self-heating is induced. A relatively high surface area to volume ratio compared with field or pilot compost piles results in high conductive and convective heat loss. In some systems, the heat generated from degrading organic substrates may not be enough to raise and maintain the thermophilic compost temperatures. It has been a common perception among composting researchers and practitioners that the minimum size of a pilot compost pile must be at least 19 to 38 m³ (25 to 50 cu yd) in order to retain the heat (Hanif 1995).

Several researchers used feedback temperature control and heating systems in order to minimize the heat loss and were able to maintain self-heating induced thermophilic conditions (Cook, Bloom, and Halback 1994; Hogan, Miller, and Finstein 1989; Magalhaes et al. 1993). Small bench-scale remediation composting systems require much more precise design and operational control in order to be successful, compared with rather insensitive but more stable pilot-scale compost piles.

The Waterways Experiment Station Adiabatic Composting System (WACS) II is a composting reactor with a sophisticated feedback temperature control and heating system. Compost Mix 7 was evaluated for the feasibility of treating soils contaminated with the explosives in actual composting environments using the WACS II system.

Materials and Methods

Bench-scale reactor system

The WACS II is a pseudo-adiabatic composter combined with instrumentation and automatic data collection (Figure 3). The composting reactor is a 14-L polyvinyl chloride cylinder insulated to reduce conductive heat transfer. This reactor is placed into a Styrofoam box to further isolate the composter from ambient temperatures. This isolation eliminates heat loss so that heat can accumulate inside the reactor, raising the composting temperature. The resistance temperature probes (RTDs) were inserted into the center of the composting reactor as well as against the inside and outside of the cylinder wall. A proportional-integral-derivative feedback temperature control system used the two reactor wall RTD measurements to track the temperature differences. The temperature of air in the Styrofoam box is maintained at the same temperature of the inside reactor wall by passing preheated or cooled water through a radiator inside the box while a fan circulates the temperature-controlled air.

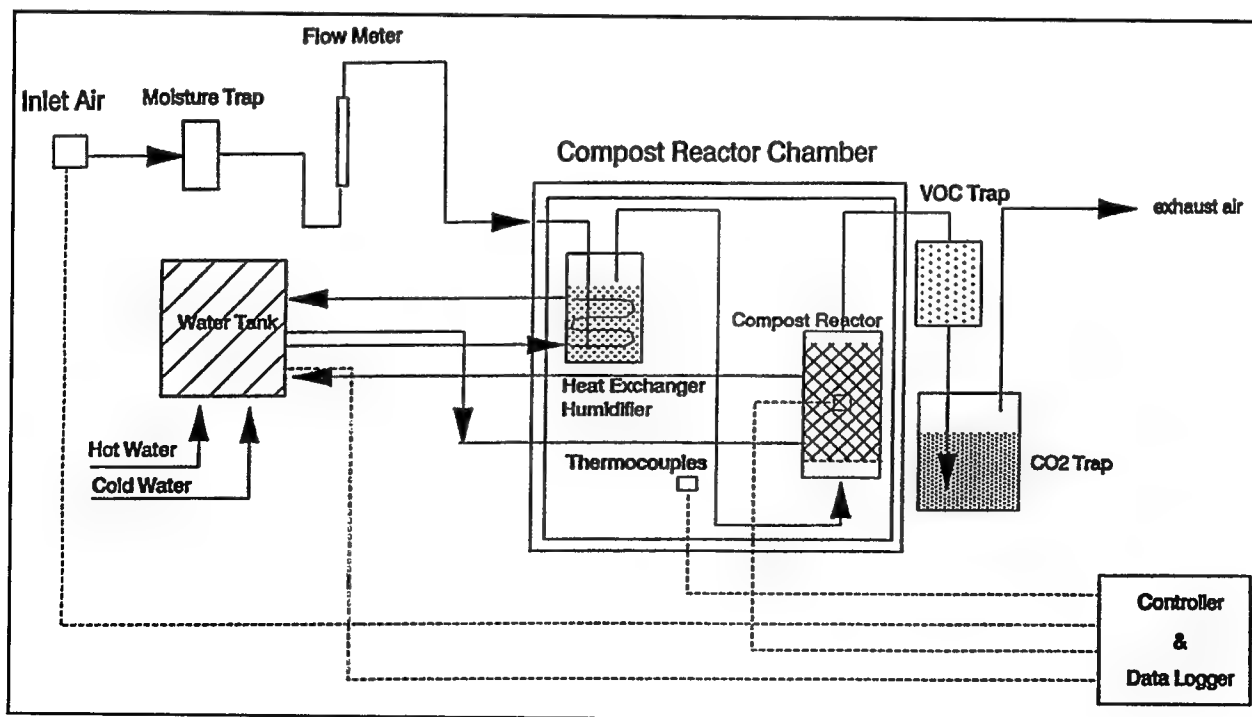


Figure 3. Schematic diagram of bench-scale batch compost reactor system

Finally, preconditioned air is supplied to the reactor to maintain aerobic respiration and to reduce convective heat loss from the composting pile through the latent heat of vaporization. Air temperature is dynamically adjusted to the temperature at the core of the composting pile. Air is also humidified before entering the reactor. Aeration events occur every 1 in 10 min if the composting temperature is less than 55 °C or continuously if the temperature is above 55 °C. Temperature readings were recorded every 2 min as well as total elapsed time for aeration events.

University of Minnesota compost reactor system

To evaluate the contaminant fate of TNT via radiolabeled method, the composting Mixture 4 was placed in a 20-L composter that is 31 cm (1 ft) in diameter and 40 cm (16 in.) in height (Figure 4). Ambient air is pulled through the system by a laboratory vacuum at a pressure of 15-17 in. of mercury. The airflow is regulated with a flow meter. A gas-drying jar containing Baralyme granules was used to dry the air and to remove some CO₂. The remaining CO₂ is removed through a 3.8-L (1-gal) jar of 1 molar of KOH solution. Passing it through a distilled water trap humidifies filtered air. The humidified air enters the bottom of the compost reactor and exits at the top. It is then condensed in a stainless steel tube coil that is cooled by a large fan. The condensed water is collected in a moisture

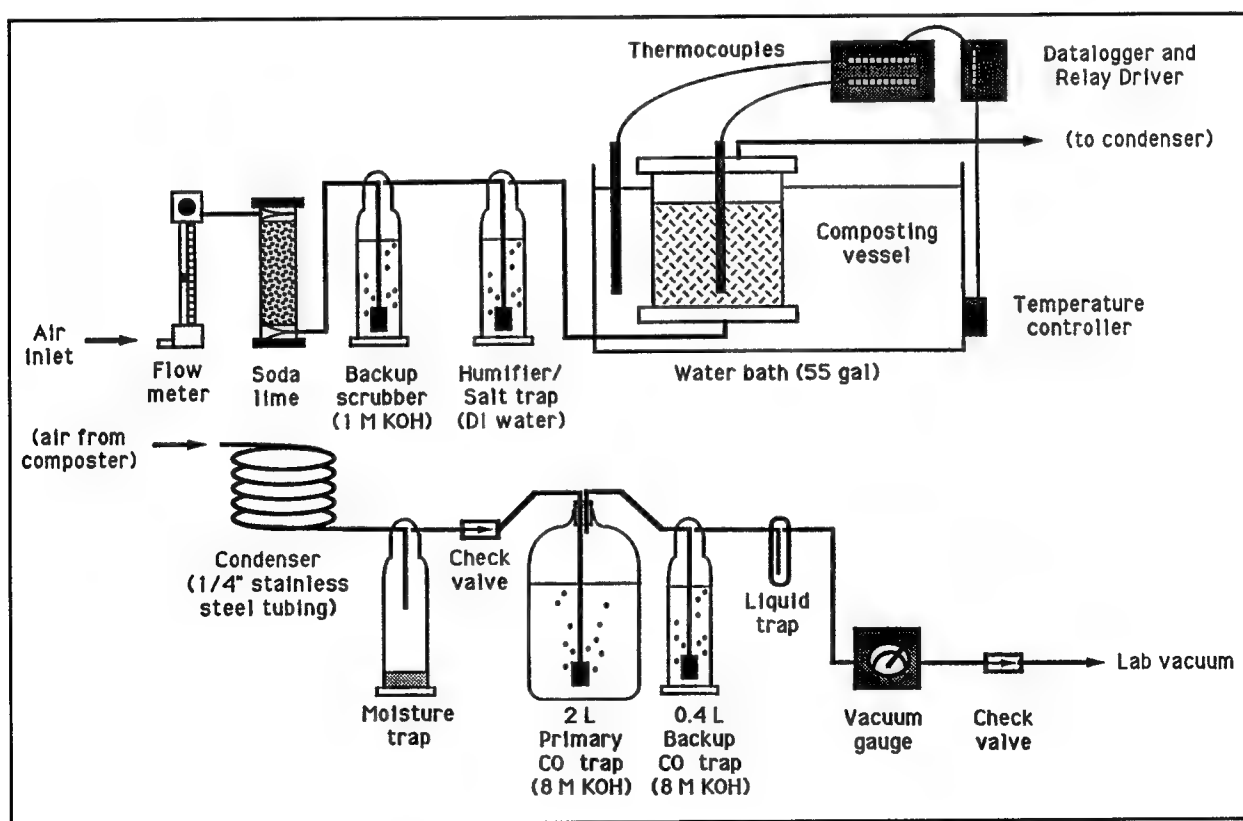


Figure 4. Schematic diagram of University of Minnesota compost reactor system (Cook, Bloom, and Halback 1994)

trap while the air passes through an organic trap consisting of foam absorbers. The CO₂ is removed from the air again in two KOH traps. The primary trap contains 1,800 ml of the KOH solution. The secondary trap contains 400 ml of KOH. After CO₂, organics, and moisture have been removed, the air passes through another moisture trap, then to the vacuum.

The reactor uses thermocouples to monitor the compost temperature. The reactor tracks temperature as well as microbial activity through O₂ and CO₂ traps in the exit airstream. Two thermocouples are used to display the temperature of the compost. One thermocouple is placed at the core of the reactor, and the other thermocouple is placed at the inside edge of the reactor. Temperatures were automatically logged.

Compost mixing procedure

The ingredients for Mixtures 3 (40-percent cow manure, 40-percent cornstalk, and 20-percent soil) and 4 (40-percent pig manure, 40-percent cornstalk, and 20-percent soil) were measured by volume, weighed, and mixed together in a 57-L (15-gal) twin-shell mixer. Table 5 shows the composition of Mixtures 3 and 4 used in the bench-scale system. Table 6 shows the composition of Mixture 4 used in the University of Minnesota compost system.

Table 5
Bench-Scale - Compost Composition of Mixtures 3 and 4

Mixture Number	Ingredient	Percent by Volume	Wet Weight, g	Percent by Wet Weight	Percent Moisture	Dry Weight g	Percent by Dry Weight
3	Cow manure	40	2,119.68	35	18	381.54	16
	Cornstalks	40	174.33	3	92	160.38	7
	Soil	20	2,884.83	49	66	1,904.00	77
	Water	—	750	13	—	—	—
4	Swine manure	40	2,118.56	37	28	593.20	22
	Cornstalks	40	173.72	3	92	159.82	6
	Soil	20	2,879.55	51	66	1,900.50	72
	Water	—	500	9	—	—	—

Table 6
Radiolabeled - Compost Composition for Mixture 4

Mixture Number	Ingredient	Percent by Volume	Dry Weight, g	Percent by Dry Weight
4	IAAP Line 1 Impoundment Soil			
	Pig manure	40	0.81	12
	Cornstalks	40	0.37	5
	Soil	20	5.59	83
	WES Reference Soil			
	Pig manure	40	0.60	9
	Cornstalks	40	0.36	6
	Soil	20	5.58	85

Results and Discussion

Bench-scale reactor system

Figure 5 compares TKN, pH, moisture content, TVS, and C/N values for Mixtures 3 and 4. The TVSs decreased approximately 22 percent for both mixtures. The TKN values showed the most significant differences between the two mixes. The TKN values increased in the cow mixture; however, the fluctuation was probably due to sampling error, so the concentration probably remained approximately constant. Meanwhile, the TKN concentration declined more than 50 percent in the pig mixture. The reduction in total nitrogen was expected to be caused by ammonia-N volatilization as well as nitrification. The moisture content remained approximately constant for the cow mixture ranging from 45.8 to 47.8 percent during the 30-day compost run, whereas the moisture content decreased from 37.6 to 26.1, indicating an enthalpy change in the system for pig

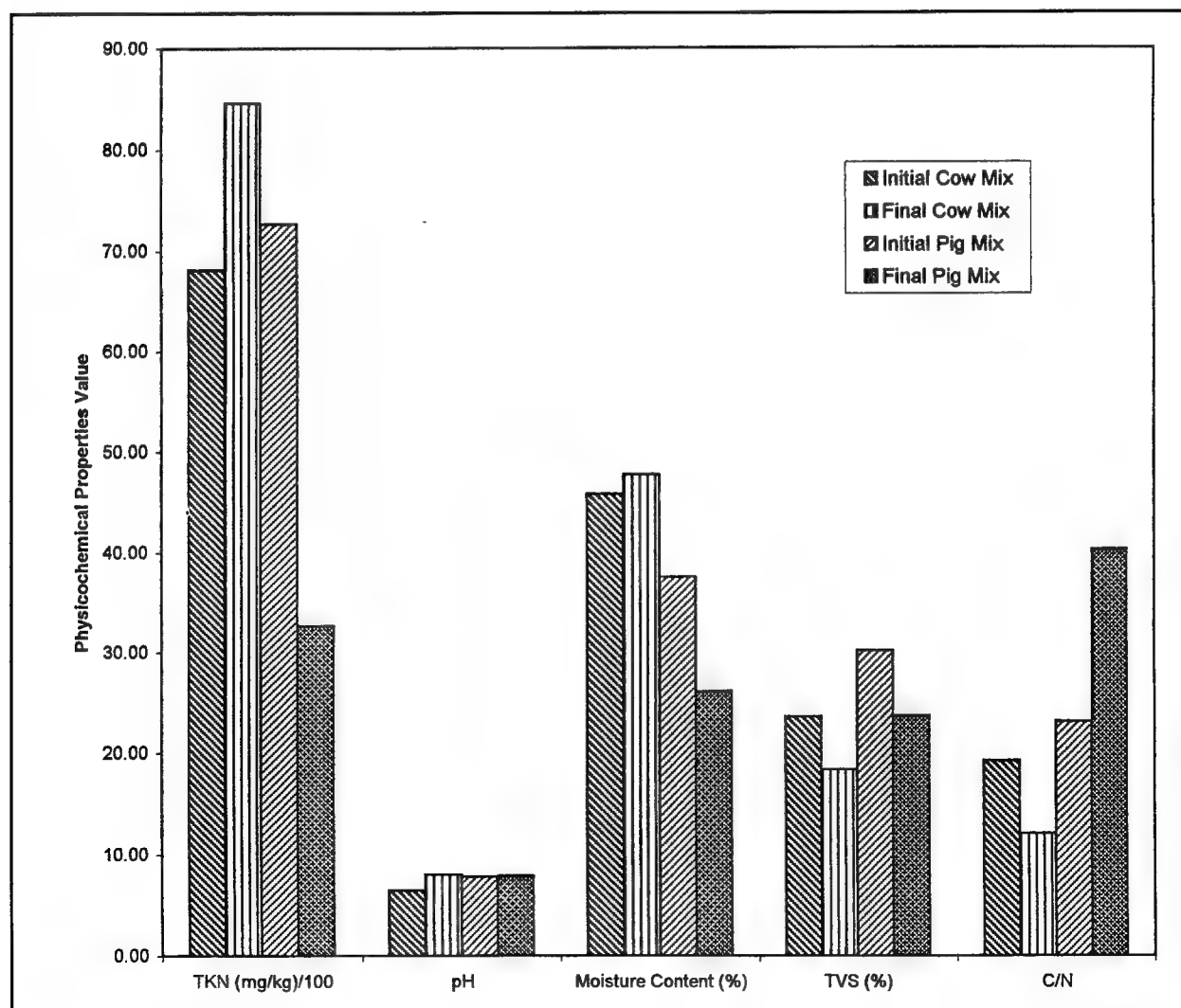


Figure 5. Physicochemical properties for Mixtures 3 and 4

manure. The pH for both mixtures remained within acceptable ranges for microbial activity. Kayhanian and Tchobanoglous (1992) state that the initial pH range for composting is 5 to 7, raises to approximately 8.5 as the compost reaches thermophilic temperatures, and settles to a pH of 7 to 8 in mature compost. The opposite trends in C/N ratio occurred between the two mixes. A decrease in C/N ratio occurs in the cow manure mixture because the TVS decreased while the TKN value remained approximately constant. Meanwhile, the C/N ratio increased in the pig manure mixture, suggesting that the nitrogen levels decreased at a faster pace than the carbon degradation process.

Figures 6 through 8 show average core temperature as well as the overall temperature profile and aeration data for Mixture 3. Core temperature profile, Figure 6, for the cow manure compost displays the average core temperature profile for 30 days. The maximum and minimum temperatures for each day are also displayed as Y error bars. Due to complications in the self-heating apparatus, the temperature controller was turned off initially for 1 day and subsequently for 8 additional days. The composting piles remained mesophilic for the first 16 days. The temperature did increase to 40 °C ranges for the next 3 days. The temperature then plummeted to under 30 °C for the rest of the run. These temperatures would allow ammonia to remain as NH_3 . Figure 7 displays the composting temperature profiles of the core, inside wall, and outside wall temperatures. The core composting temperature was slightly higher than the wall temperature, showing radial heat loss through the reactor. The feedback temperature control system maintained the outside wall temperature and

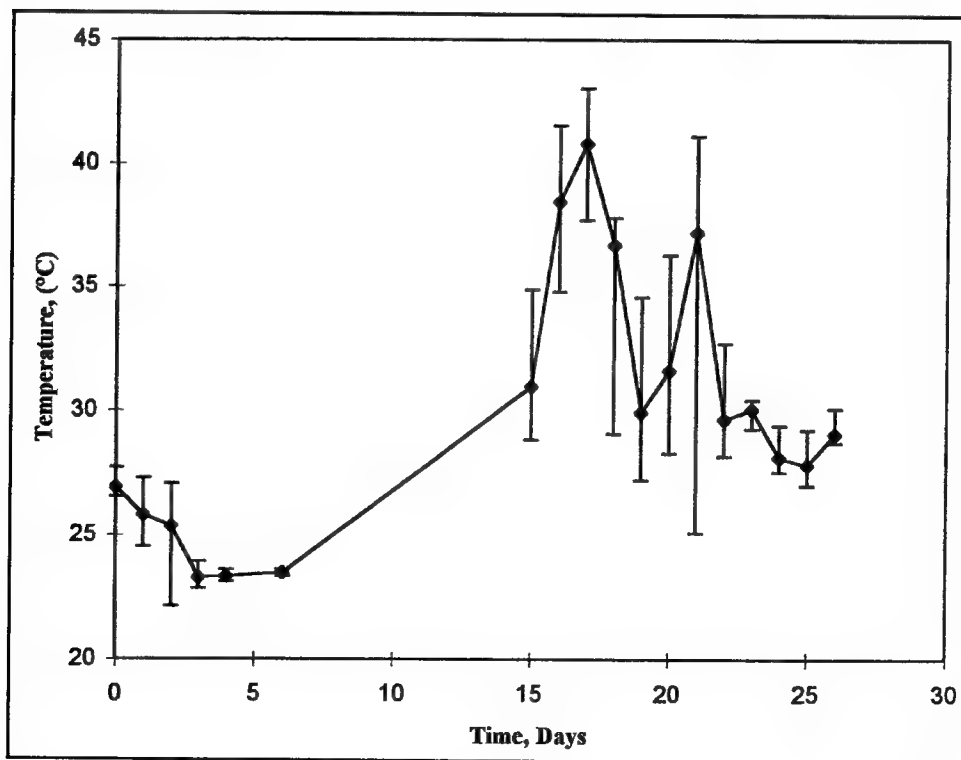


Figure 6. Cow mixture core temperature profile

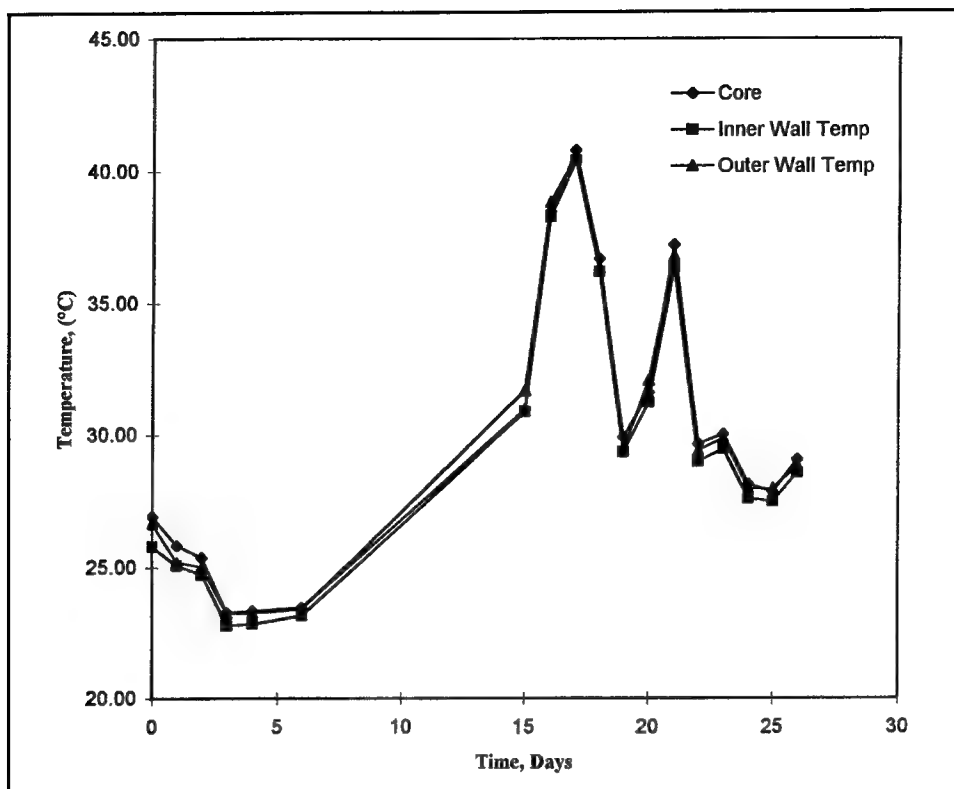


Figure 7. Cow mixture overall process temperature profile

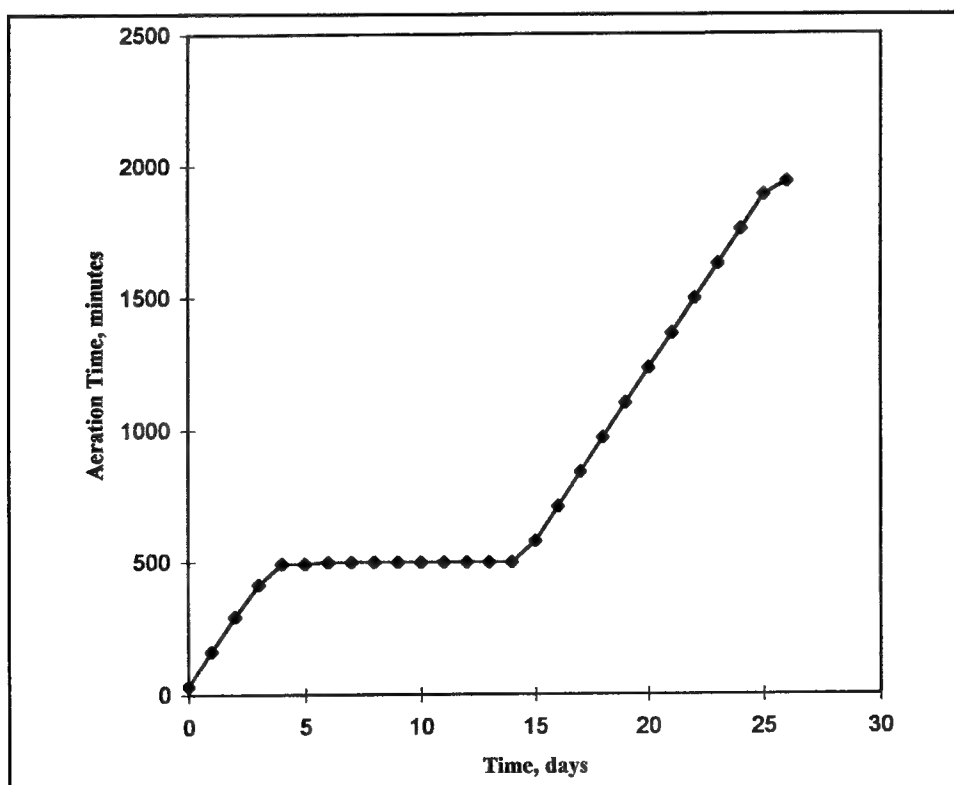


Figure 8. Cow mixture cumulative aeration

inside wall temperature perfectly, ensuring adiabatic conditions. Figure 8 shows the cumulative aeration minutes. During Days 6 through 15, no oxygen was added to the system. These anaerobic conditions may have had effect on the TKN values by producing a significant amount of nitric acid. Adding air to the system on Day 16 may have allowed some rapid depletion of carbon, increasing the temperature until the readily available carbon was exhausted lowering the temperature. The overall accumulated air, Figure 8, was 1,936 min at 3.78 L/min. Air was exchanged 522 times throughout this run. Haug (1993) estimated that a yard waste composting pile with 80-percent TVS and 50-percent degradability would require 1,510 exchanges. Since the degradability rate of cow mixture was 4 percent and the flow rate was higher, the number of exchanges for this composting run should be lower. The overall aeration for this composting run was 0.53 m³/kg VS-day.

Figures 9 through 12 display the average core temperature as well as the overall temperature profile and aeration data for the pig mixtures (Mixture 4). Figure 9 shows the average core temperature profile of the pig compost for 30 days. The maximum and minimum temperatures for each day are also displayed as Y error bars. The composting piles reached a thermophilic temperature range within the first 24 hr; however, the failure in the temperature control system limited the heat accumulated, causing a decline in temperature. The temperamental behavior of the temperature control system continually retarded the self-heating capacity of the compost until the readily available carbon diminished after Day 20. Even

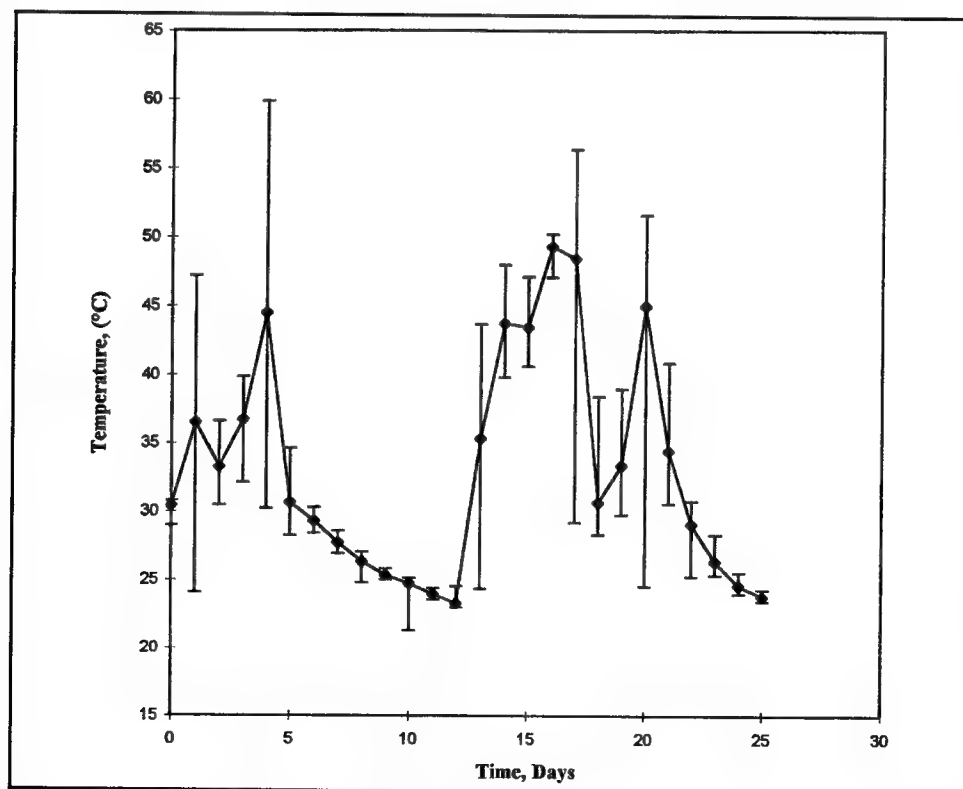


Figure 9. Pig mixture core temperature profile

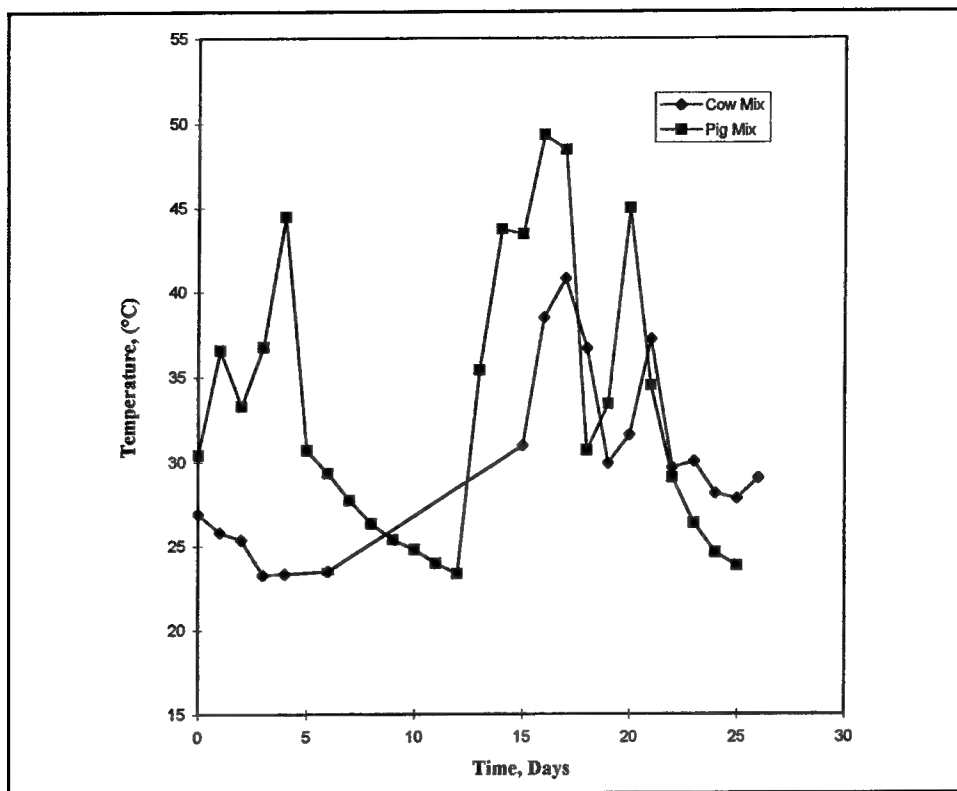


Figure 10. Comparison of cow and pig mixture core temperature

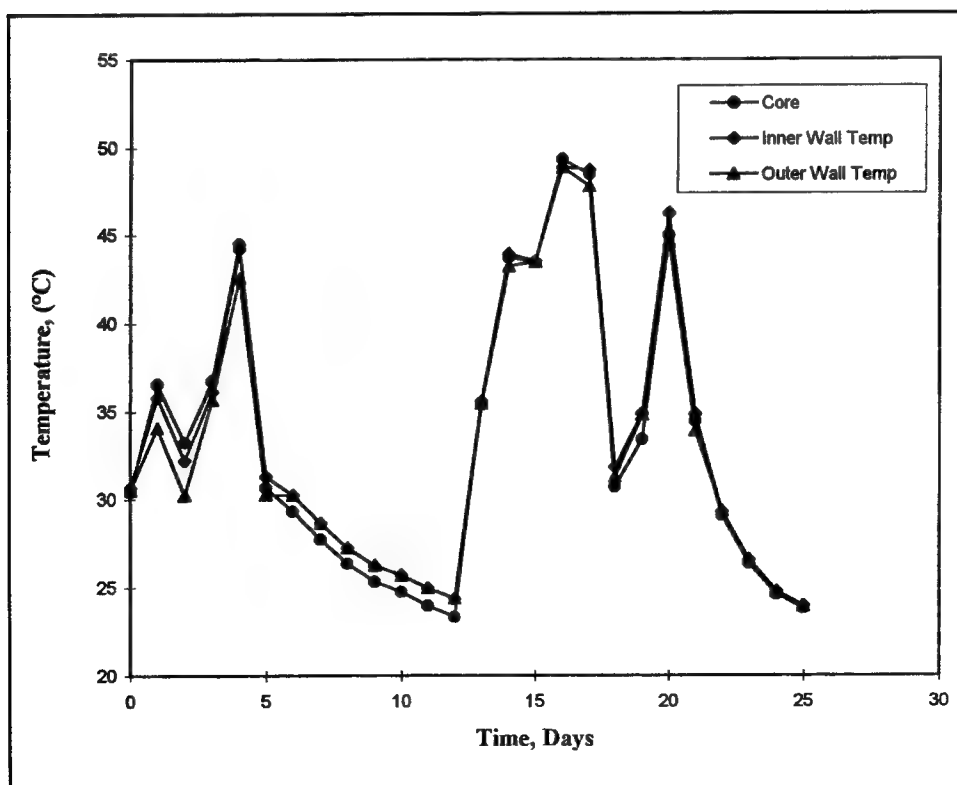


Figure 11. Pig mixture overall process temperature profile

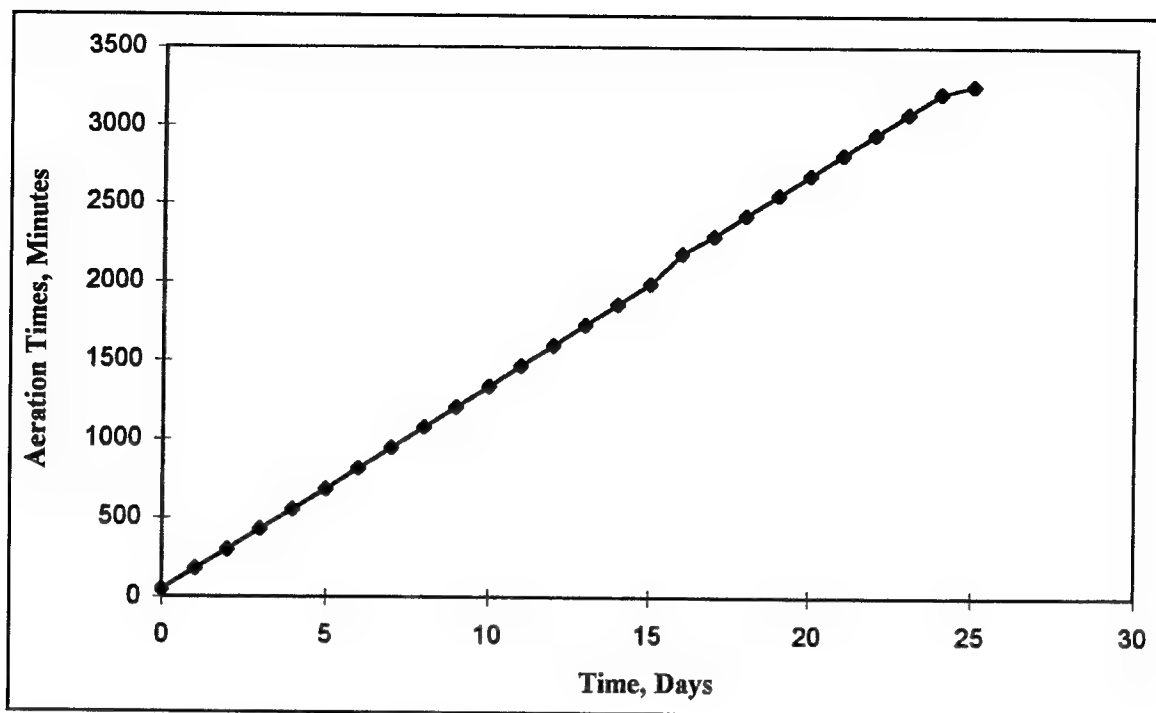


Figure 12. Pig mixture cumulative aeration

though the temperature fluctuated during this experiment, the temperature profile achieves the goals of field-scale composting by accumulating heat, raising the temperature of the pile, and reducing temperatures after several days. This compost run conformed to the USEPA regulations that the compost temperature must maintain a temperature of 40 °C for at least 5 days and reach a temperature of 55 °C for a 4-hr period. The compost pile reached thermophilic temperatures for at least 8 days. Figure 10 compares the average core temperature for the cow and pig mixtures. Figure 10 shows the compost temperature of pig mixture extended that of the cow mixture. Figure 11 shows the overall temperature profiles for the pig manure, and it displays similar trends to that of the cow manure compost. Again, the core composting temperature was higher than the wall temperature, showing radial heat loss through the reactor. Figure 12 shows cumulative aeration for this compost run. Day 16 had the highest aeration using 193 min of air at a rate of 3.78 L/min. The number of aeration minutes corresponded well to the temperature profile. The overall accumulated air was 3,253 min. Air was exchanged 878 times throughout this run. The overall aeration for this composting run was 0.65 m³/kg VS-day.

Figure 13 shows the degradation of HMX and RDX concentrations. TNT, 4A-DNT, and 2A-DNT concentrations were undetected in both the cow and pig mixtures (Table 7). The cow mixture also showed no significant concentration reduction in HMX and RDX. The lack of reduction of explosive concentration in the cow mixture was expected since there was no significant heat accumulation in the mix and a limited supply of air. WES has used cow manure in other composting mixtures and also seen no

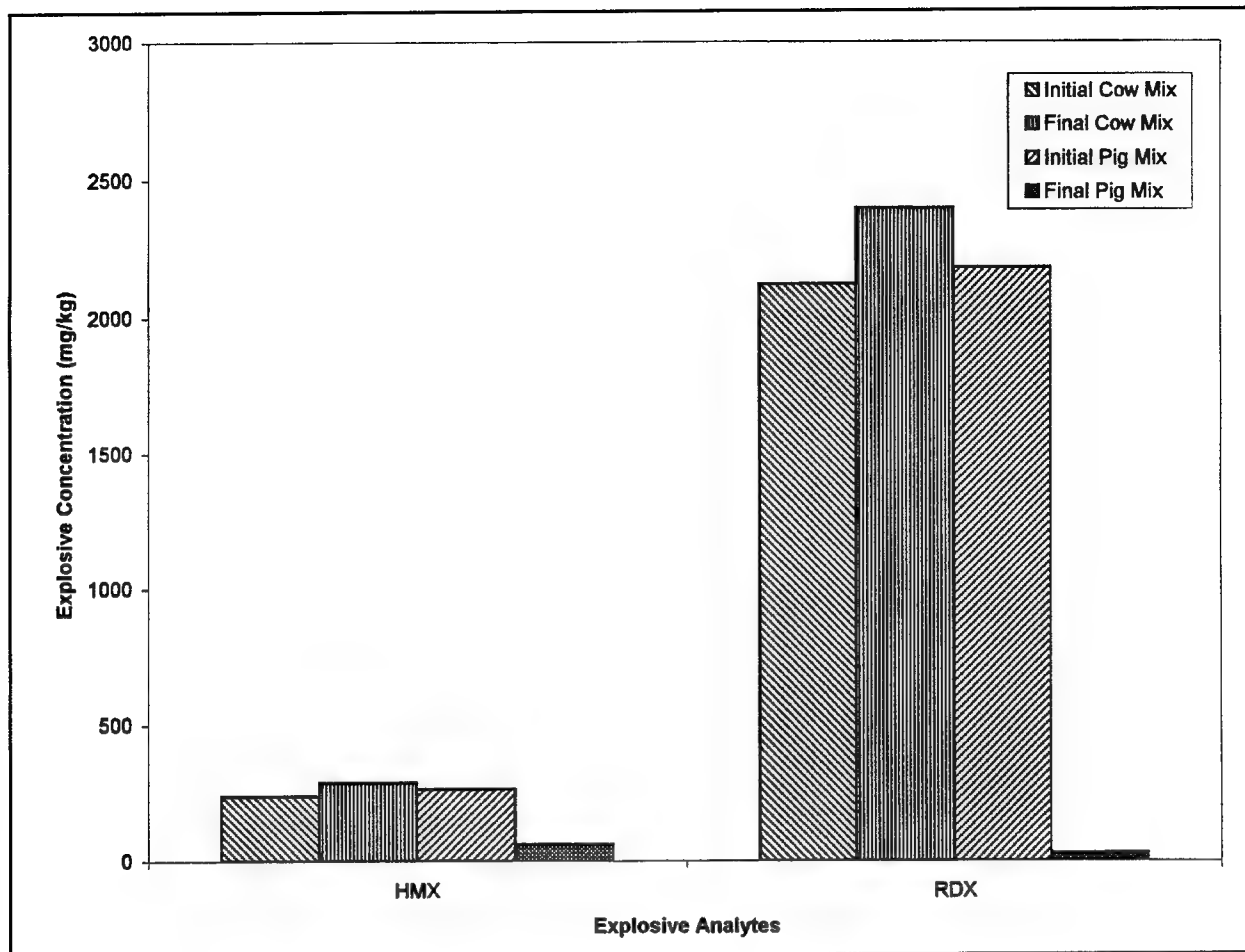


Figure 13. Average explosive analysis results for Mixtures 3 and 4

Table 7
Bench-Scale - Explosive Analysis for Mixtures 3 and 4

Mixture Number	Sample No.	Explosive Concentrations, mg/kg				
		TNT	RDX	HMX	2A-DNT	4A-DNT
3	Day 0	19.3J	2,120	240	BDL	8.00
	Day 30, Replicate 1	15.8J	2,480	288	12.4	8.09
	Day 30, Replicate 2	22.0J	2,600	321	14.6	9.77
	Day 30, Replicate 3	19.7J	2,110	260	13.2	9.31
	Average	19.2J	2,397	290	13.4	9.06
4	Day 0	15.2J	2,180	266	BDL	5.10
	Day 30, Replicate 1	14.4J	23.6	49.9	11.0	6.43
	Day 30, Replicate 2	25.9	39.0	81.4	13.1	8.11
	Day 30, Replicate 3	15.9J	23.7	57.5	12.5	6.08
	Average	18.7J	28.8	62.9	12.2	6.87
Soil	Replicate 1	20.4J	973	138	11.5	5.50
	Replicate 2	58.5	4,290	510	40.6	19.2
	Replicate 3	44.0	3,360	423	31.4	15.6
	Replicate 4	28.6	2,560	316	23.7	12.4
	Average	37.9	2,796	347	26.8	13.2

NOTE: BDL — Below Detection Limit; J — estimated value less than detection limit.

reduction in HMX (Preston, Seiden, and Ro 1997). However, the pig manure mixture showed significant reduction for both HMX and RDX concentrations. The initial and final values for HMX was 266 and 63 mg/kg, respectively (77-percent reduction). RDX concentration was diminished by 98.7 percent.

University of Minnesota compost reactor system

Based on the bench-scale study results, WES determined the best compost mix for degrading explosives in IAAP soil was Mixture 4. To ensure that the mix was acceptable, WES had to prove the pig compost mixture would rise to thermophilic temperatures. In addition, WES wanted to identify if any temperature differences occurred using IAAP Former Line 1 Impoundment soil and WES' reference soil.

The experiment was to compare elevation in temperature between explosives-contaminated soil and WES' reference soil. IAAP Former Line 1 Impoundment soil was used in this first experiment as well as WES' reference soil as the blank. This experiment lasted 30 days. The dry weights for this mixture had about 2.5 times more soil than the composts prepared in the previous study. This corresponds to about 84 percent by dry weight for the mixes.

Figure 14 compares O_2 and CO_2 headspace rates for the TNT-contaminated soil and the WES' reference soil. The decline in oxygen corresponds well with the increase production rate of CO_2 for both soils. In addition, the figure shows that most of the biological activity ceases after 15 days of composting. Figure 14 also shows that the WES' reference soil produced a higher amount of CO_2 . However, both soils show a different rate of oxygen uptake and CO_2 mineralized. Figure 14 shows that the microorganism within composts for the TNT soil and WES' reference soil has an increase in consumed oxygen beginning at Day 4 and Day 8, respectively. Similar patterns are displayed for the rate of CO_2 production. Figure 15 shows the temperature profiles of each soil type having the same trends; however the reference soil maintained higher temperatures once 50 °C was reached.

Figure 16 shows the initial and final concentrations of TNT in milligrams of TNT per kilogram of compost (mg/kg). The initial concentration of TNT of 513 mg/kg reduced to 14 mg/kg (97-percent reduction). The half-life of TNT degradation for this mixture was 5.77 days.

The second experiment compared composts with and without radiolabeled TNT. The components and dry weights for this run are shown in Table 6. The total weights of both mixers are approximately equal. The unlabeled compost weighed in at 3.40 kg and the labeled compost at 3.41 kg. The soil comprised about 85 percent of the dry weight.

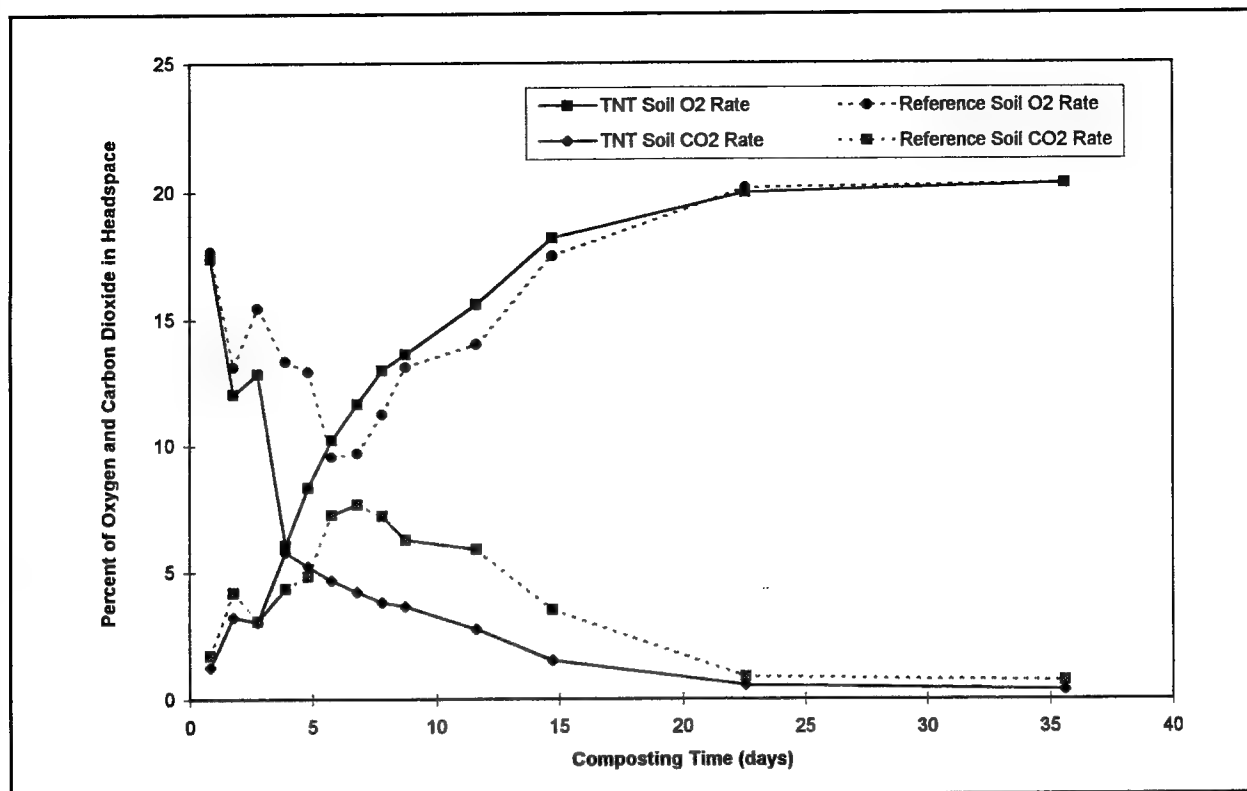


Figure 14. University of Minnesota O₂ and CO₂ headspace rates

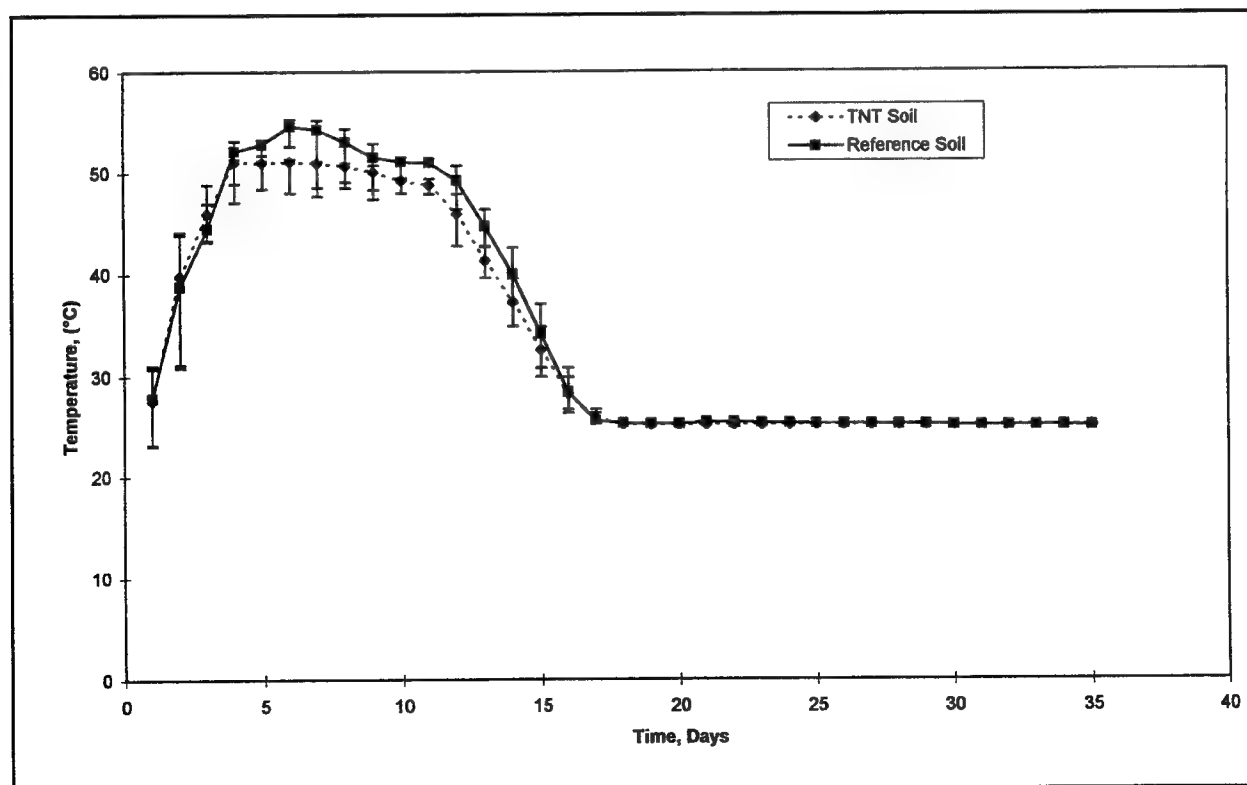


Figure 15. University of Minnesota core temperature profile

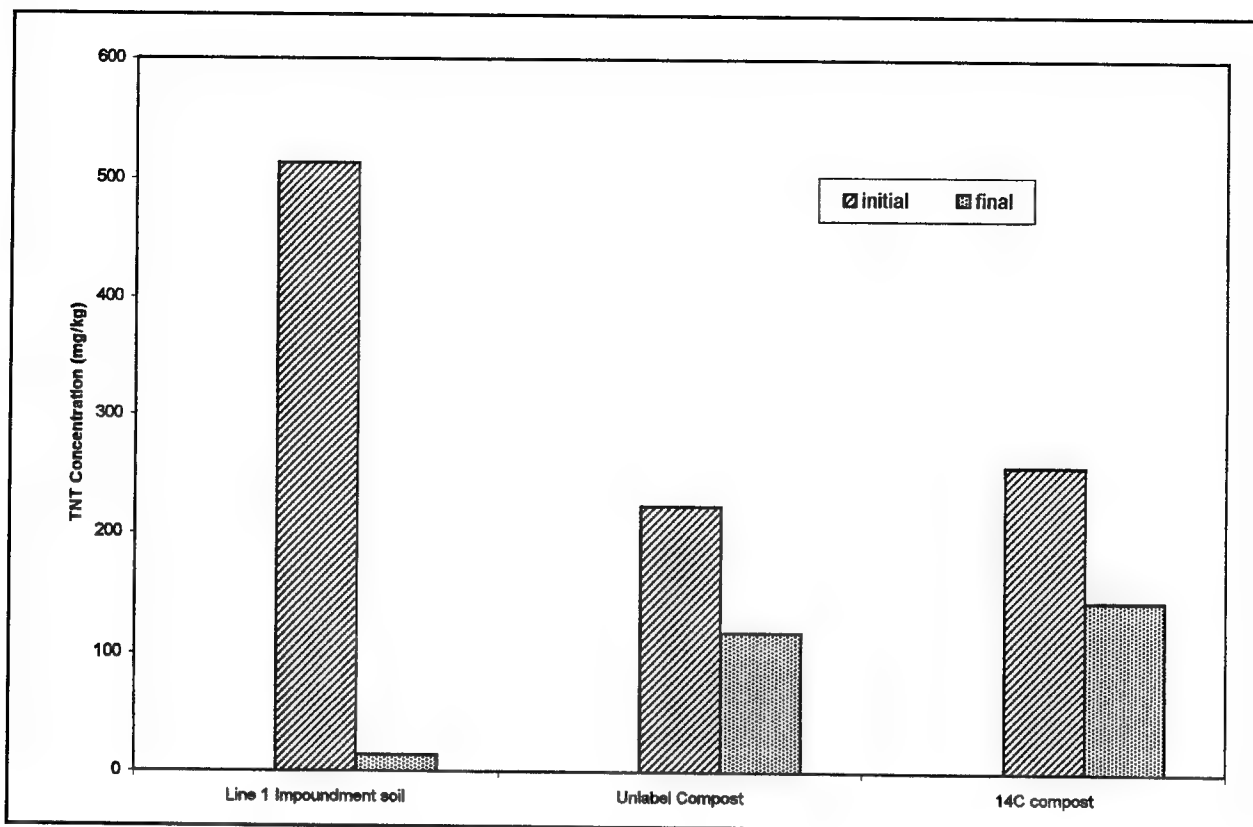


Figure 16. University of Minnesota initial and final TNT concentration

Figure 17 compares O_2 and CO_2 headspace rates for the unlabeled and labeled TNT-contaminated soil. The decline in oxygen corresponds well with the increase production rate of CO_2 for both soils. Figure 17 also shows that most of the biological activity ceases after 15 days of composting. Figure 18 shows the temperature profiles of each soil type having the same trends. Figures 17 and 18 show little difference in the unlabeled and labeled TNT respiration rate and temperature profile, respectively.

Figure 16 also shows the initial and final concentrations of unlabeled and labeled TNT. Radiolabeled and unlabeled TNT concentrations were reduced by 44 and 47 percent, respectively.

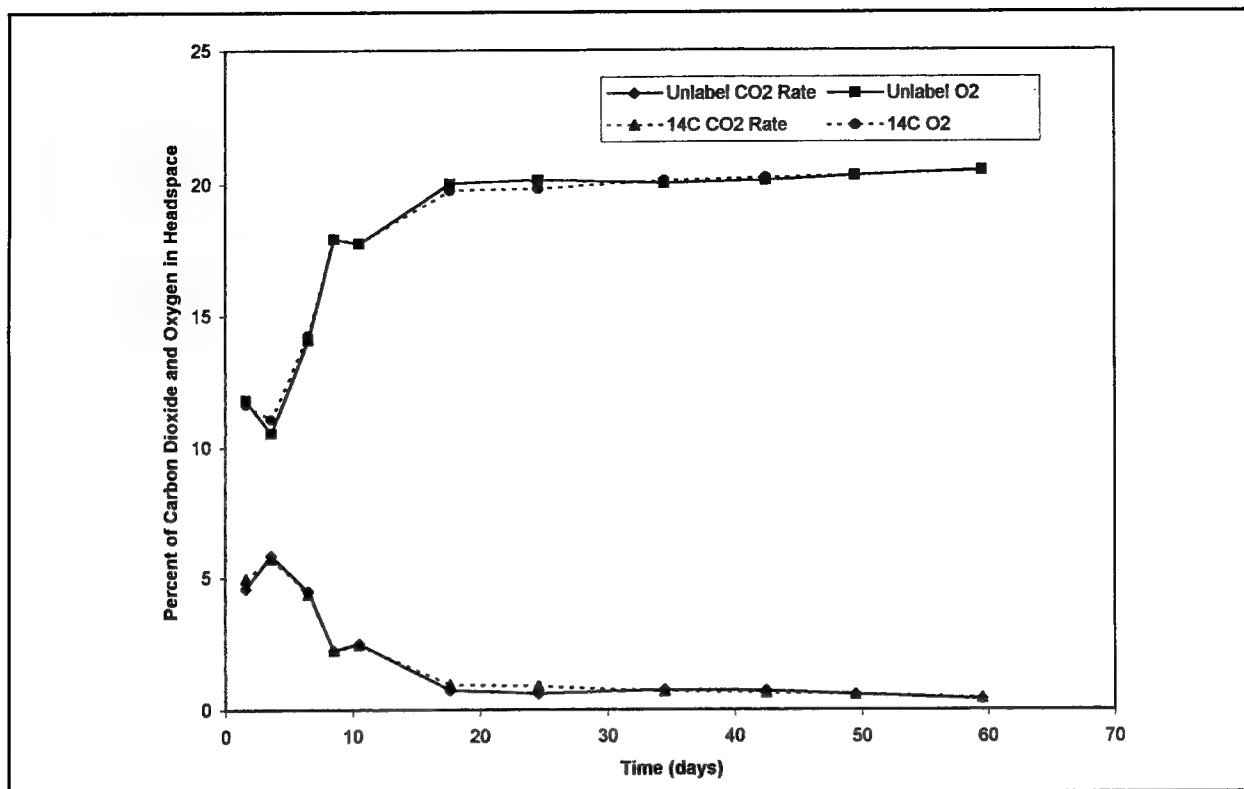


Figure 17. Radiolabeled O₂ and CO₂ headspace rates

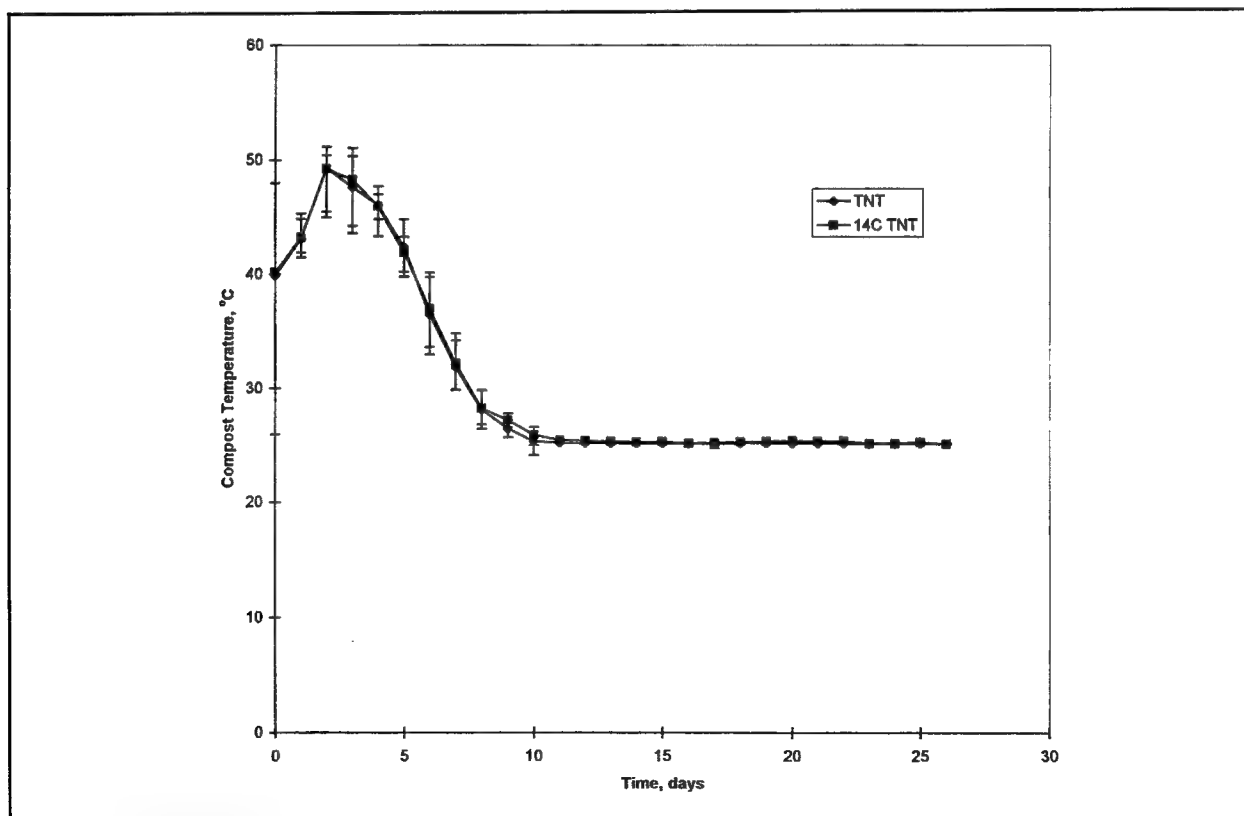


Figure 18. Radiolabeled core temperature profile

5 Conclusions and Recommendations

Conclusions

Mixtures or various combinations of amendments and bulking agents were evaluated for composting using the respirometer as a screening tool. The bench-scale composting with the compost mixture selected from the respirometry was used to test the effectiveness of explosive-compound removal in actual composting environments.

Based on the results of the respirometric, bench-scale, and pilot-scale compost, the following is concluded:

- a. The locally available amendments were cow manure and pig manure. The locally available bulking agents were sawdust, cornstalk, and wood chips.
- b. Of eight compost mixes used in the respirometric study, Mix 3 (40-percent cow manure, 40-percent cornstalk, and 20-percent soil) and Mix 4 (40-percent pig manure, 40-percent cornstalk, and 20-percent soil) were ranked the highest.
- c. Although Mix 6 was effective in removing explosives from the respirometric study at 40 °C, SBR and the maximum OURs of Mixtures 3 and 4 were the highest among the eight mixtures, respectively. Therefore, Mixtures 3 and 4 were selected for subsequent bench-scale compost study.
- d. The bench-scale composting study had an overall average rate of aeration of 0.53 and 0.65 m³ air/kg VS-day for Mixtures 3 and 4, respectively. The moisture content remained approximately constant ranging from 45.8 to 47.8 percent and decreased for Mixture 4 ranging from 37.6 to 26.1 percent.

- e.* TKN values continuously decreased over the entire composting period. Several reasons may be volatilization loss of ammonia-N during initial composting phase and nitrification during final phase of composting. The decrease in TKN during the later stage of composting resulted in increase in C/N ratio from 30.7 on Day 15 to 34.7 on Day 35.
- f.* The majority of the explosive and transformation product concentrations using the WACS II system was reduced within the first 15 days of composting. Compost Mix 3 did not reduce the HMX concentration compared with the compost Mix 4.
- g.* The University of Minnesota experiments show that the pig compost mix allows the temperature to be elevated to thermophilic temperatures. Therefore, the mix will be sufficient to degrade HMX and RDX as well as provide significant reduction in explosive concentrations.
- h.* The radiolabeled TNT studies showed little difference between unlabeled and labeled TNT respiration rate and temperature profile.
- i.* The reduction in TNT concentration was 47 and 44 percent for unlabeled and labeled TNT, respectively.

Recommendations

Based on the results of this study, it is recommended that Mix 4 be utilized in the pilot-scale study at IAAP sites. Mixes 3 and 6 may also be proven to be beneficial in a pilot-scale study. Toxicity studies should be conducted to relate the remediation composting engineering design and operation to the quality of compost in terms of target chemical removal and toxicity reduction.

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13. ABSTRACT (Maximum 200 words) <p>Bench-scale compost and radiolabeled studies were conducted at the U.S. Army Engineer Waterways Experiment Station (WES) and at the University of Minnesota to evaluate the reduction of explosives-contaminated soil at Iowa Army Ammunition Plant. The goal of the study was to evaluate and to select the best combination of amendments, contaminated soils, and bulking agents to be utilized in the compost technology for remediation of explosives-contaminated soils. The respirometric test was utilized as a screening tool to provide a general indication of biological activity within eight compost mixtures. The bench-scale compost reactor test was to extend the respirometric study by evaluating the applicability of the screened compost mixtures. The radiolabeled study was to provide insight into the apparent degradation of the explosive contaminant during the composting process. The respirometer results showed that cow manure and corn stalk (Mixture 3) and swine manure and corn stalk (Mixture 4) mixtures outperformed the other mixtures. Mixture 3 showed the best biodegradation rate; Mixture 4 showed the best respiration rate, while its biodegradation rate falls approximately within the middle of the eight treatments. Therefore, Mixtures 3 and 4 were advanced to the bench-scale composting test. The bench-scale composting study validated the explosive removal capacity of Mixtures 3 and 4. Mixture 3 temperature reached the mesophilic range (40 °C), while Mixture 4 temperature reached the thermophilic range (50 °C). The compost mixtures</p> <p style="text-align: right;">(Continued)</p>																
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returned to ambient temperature after 10 days of composting. The majority of the explosives and transformation products were removed within 15 to 20 days of composting. These results also show that Mixture 3 showed no significant concentration reduction in HMX and RDX probably because of significant heat accumulation in the mix. However, Mixture 4 showed a 77- and 99-percent reduction in HMX and RDX, respectively. The TNT radiolabeled test was conducted on the composted material of Mix 4 and a WES reference soil. These tests were used to prove that Mix 4 would rise to thermophilic temperatures and to determine if any temperature differences would occur between the labeled and unlabeled soils. The radiolabeled TNT studies showed little difference between unlabeled and labeled TNT respiration rate and temperature profile. The results show that the temperature profiles remained at the thermophilic range for approximately 7 days. The TNT concentration was reduced by 97 percent in the Line 1 Impoundment soil. The reduction in TNT concentration was 47 and 44 percent for unlabeled and labeled TNT, respectively.